ORGANOMETALLICS

Photocleavage of Coordinated NO under Visible Light from Two Different Classes of Organometallic Ruthenium Nitrosyl Complexes: Reversible Binding of Phenolato Function[†]

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Supporting Information

ABSTRACT: The structurally similar Ru(III) complexes $[Ru(L^{SB1})(PPh_3)_2Cl]$ (1), where $L^{SB1}H_2 = 2$ -(4-chlorobenzylidineamino)phenol and H = dissociable protons, and $[Ru(L^{AZ1})-(PPh_3)_2Cl]$ (2), where $L^{AZ1}H_2 = 4$ -methyl-2-(*p*-tolyldiazenyl)phenol and H = dissociable protons, were reacted with in situ generated NO derived from acidified nitrite solution. These reactivity studies on 1 and 2 afforded the complexes $[Ru(L^{SB2}H)-(PPh_3)_2(NO)Cl](ClO_4)$ (1a) and $[Ru(L^{AZ2}H)(PPh_3)_2(NO)Cl]-(ClO_4)$ (2a), respectively, where $L^{SB2}H = 2$ -(4-chlorobenzylidineamino)-4-nitrophenol, $L^{AZ2}H = 4$ -methyl-2-nitro-6-(*p*-tolyldiazenyl)phenol, and H = dissociable proton. Complexes 1a and 2a



were found to be diamagnetic and were characterized by ¹H and ³¹P NMR spectral studies. Both **1a** and **2a** exhibited v_{NO} bands near 1800 cm⁻¹ in their IR spectra. The molecular structures of $1a \cdot CH_2Cl_2 \cdot 3H_2O$ and $2a \cdot 2H_2O$ were determined by X-ray crystallography, and NO coordination as well as ligand nitration were authenticated from the crystal structure. In both of the nitrosyl complexes coordinated NO was found to be photolabile under visible light and photocleaved NO was transferred to reduced myoglobin. The photolability of NO in **1a** and **2a** afforded the complexes [Ru(L^{SB2})(PPh₃)₂Cl] (**1b**) and [Ru(L^{AZ2})(PPh₃)₂Cl] (**2b**), respectively, and the molecular structure of **1b** · 2CH₂Cl₂ was confirmed by an X-ray crystal structure solution. A novel type of reversible binding of the phenolato function to the metal center was revealed during NO coordination and photocleavage.

INTRODUCTION

There has been considerable current interest in studies on the interaction of nitric oxide (NO) with transition-metal complexes. $^{1-3}$ Nitric oxide, a diatomic radical species, is an important signaling molecule in a variety of biological processes such as vasodilatation, immune response, neurotransmission, apoptosis, etc. in different cells and tissues.⁴ In biosystems, NO is synthesized by nitric oxide synthase (NOS) enzyme and several concentration-dependent activities of NO were discovered.⁵ Hence, a particular amount of and target specific delivery of nitric oxide and scavenging of nitric oxide⁶ by transition-metal complexes are important areas in chemical research. Complexes which could deliver NO upon illumination with light are important for photodynamic therapy.⁷ Our interest originated from the synthesis of novel organometallic ruthenium nitrosyl complexes which could deliver NO on demand, because these types of complexes are scarce.8 Recently we have communicated a novel example of such a complex, where photoinduced NO delivery was observed under visible light.⁹ In recent reviews by Mascharak and co-workers³ and Pfeffer and co-workers,¹⁰ ruthenium cyclometalate complexes were not mentioned for photoinduced delivery of nitric oxide.

As part of our ongoing research on metal nitrosyl complexes,^{9,11} we have been studying the reactivity of acidified nitrite solution Scheme 1



with two different classes of structurally similar organometallic ruthenium(III) complexes (shown in Scheme 1). 12,13

In the present work, we describe the synthesis and characterization of the novel σ -aryl ruthenium nitrosyl complexes $[\operatorname{Ru}(L^{\operatorname{SB2}}H)(\operatorname{PPh}_3)_2(\operatorname{NO})\operatorname{Cl}](\operatorname{ClO}_4)$ (1a, where $L^{\operatorname{SB2}}H = 2$ -(4-chlorobenzylidineamino)-4-nitrophenol and H = dissociable proton) and $[\operatorname{Ru}(L^{\operatorname{AZ2}}H)(\operatorname{PPh}_3)_2(\operatorname{NO})\operatorname{Cl}](\operatorname{ClO}_4)$ (2a, where

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 $L^{AZ2}H = 4$ -methyl-2-nitro-6-(*p*-tolyldiazenyl)phenol and H = dissociable proton) derived from $[Ru(L^{SB1})(PPh_3)_2Cl]$ (1) and $[Ru(L^{AZ1})(PPh_3)_2Cl]$ (2), respectively, where $L^{SB1}H_2 = 2$ -(4-chlorobenzylidineamino)phenol, $L^{AZ1}H_2 = 4$ -methyl-2-(*p*-tolyldiazenyl)phenol, and H = dissociable protons (Schemes 1 and 2). Molecular structures of the resultant complexes $1a \cdot CH_2Cl_2$. $3H_2O$ and $2a \cdot 2H_2O$ were determined by X-ray crystallography. Ligand nitration in the phenyl ring containing the phenolato function was also observed in the nitrosyl complexes. Photolability of the coordinated NO in the nitrosyl complexes upon illumination of visible light was examined, and the liberated nitric oxide was trapped by reduced myoglobin. We isolated the complexes $[Ru(L^{SB2})(PPh_3)_2Cl]$ (1b) and $[Ru(L^{AZ2})$ - $(PPh_3)_2Cl]$ (2b) obtained after the photorelease of coordinated NO, and the molecular structure of one of the resultant complexes was authenticated by single-crystal X-ray diffraction. The dissociation of the ruthenium-phenolato bond and re-establishment of the same bond, respectively, during the coordination and photorelease of NO will be scrutinized in this report.

RESULTS AND DISCUSSION

Synthesis. The precursor complexes $[Ru(L^{SB1})(PPh_3)_2Cl]$ (1) and $[Ru(L^{AZ1})(PPh_3)_2Cl]$ (2) were synthesized according to the procedures reported by Chakravorty and co-workers.^{12,13} These complexes were reacted with in situ generated NO derived from acidified NaNO₂ solution. The formation of an orangeyellow color was observed when dichloromethane solutions of 1 (purple) and 2 (green) were treated with acidified NaNO₂ solution with continuous stirring for 1 h. We expected the substitution of Cl⁻ with the noninnocent ligand NO, and hence we added ClO₄⁻ ion to stabilize the large cationic ruthenium complexes $[Ru(L^{SB2}H)(PPh_3)_2(NO)Cl](ClO_4)$ (1a) and $[Ru-(L^{AZ2}H)(PPh_3)_2(NO)Cl](ClO_4)$ (2a), derived from 1 and 2, respectively. The nitrosyl complexes 1a and 2a were both recrystallized from a dichloromethane–methanol mixture. Complexes 1a and 2a were highly soluble in nonaqueous solvents such as dichloromethane, acetonitrile, dimethylformamide, and methanol; however, lower solubility was observed in water.

Photodissociation of coordinated NO from the nitrosyl complexes **1a** and **2a** afforded two more complexes: $[Ru(L^{SB2})-(PPh_3)_2Cl]$ (**1b**) and $[Ru(L^{AZ2})(PPh_3)_2Cl]$ (**2b**), respectively. It has been found that **1a** and **2a** could be synthesized again from **1b** and **2b**, respectively, using acid nitrite solution (vide infra). No reactivity was observed for precursor complexes with acidified water solution without NaNO₂.

Description of Structures. The molecular structures of complexes $1a \cdot CH_2Cl_2 \cdot 3H_2O$, $2a \cdot 2H_2O$, and $1b \cdot 2CH_2Cl_2$

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Figure 1. ORTEP diagram (50% probability level) of the cation of complex $1a \cdot CH_2Cl_2 \cdot 3H_2O$. All hydrogen atoms and solvent molecules are omitted for clarity.



Figure 2. ORTEP diagram (50% probability level) of the cation of complex $2a \cdot 2H_2O$. All hydrogen atoms and solvent molecules are omitted for clarity.

are depicted in Figures 1-3, respectively. The matrix parameters of these three complexes are described in Table 1, and selected bond distances and bond angles are given in Table 2.

[Ru(L^{SB2} H)(PPh₃)₂(NO)CI]CIO₄ (1a·CH₂Cl₂·3H₂O) and [Ru-(L^{AZ2} H)(PPh₃)₂(NO)CI]CIO₄ (2a·2H₂O). The molecular structure of 1a·CH₂Cl₂·3H₂O revealed several interesting aspects of this resultant complex. Contrary to our expectations, we found that the Cl⁻ ion was still bound to the metal center. The carbanion



Figure 3. ORTEP diagram (50% probability level) of complex $1b \cdot 2CH_2Cl_2$. All hydrogen atoms and solvent molecules are omitted for clarity.

(C(37)), Cl(1), NO, and imine nitrogen (N(1)) constituted the equatorial plane, whereas the phosphine groups occupied the trans positions. Thus, the geometry around the metal center was distorted octahedral. Interestingly, in $1a \cdot CH_2Cl_2 \cdot 3H_2O$, the phenolato oxygen was no longer bound to the metal center and picked up a proton from the reaction mixture, affording a phenolic –OH function. Hence, the tridentate ligand became bidentate in the σ -aryl ruthenium nitrosyl complex $1a \cdot CH_2Cl_2 \cdot 3H_2O$. The phenyl ring containing the phenolic –OH function became tilted and made an angle of ~50° with the ligand binding plane. The Ru–N_{NO} distance (1.787 Å) was longer than the reported values, ^{14–16} which may be due to the trans effect of the carbanion (C(37)).¹³ However, this value was smaller than the value reported by Crutchley and co-workers.¹⁷

The molecular structure of $2a \cdot 2H_2O$ was found to be similar to the crystal structure of $1a \cdot CH_2Cl_2 \cdot 3H_2O$. In $2a \cdot 2H_2O$, the carbanion (C(37)), Cl1, NO and imine nitrogen (N(1)) constituted the equatorial plane and phosphine groups were oriented along the axial positions. In $2a \cdot 2H_2O$, the phenolato oxygen became detached from the metal center and the ligand became bidentate with carbanion and azo-N donation. The phenyl ring containing the phenolato function made an angle of ~56° with the ligand binding plane.

	1a	2a	1b		
empirical formula	C ₅₀ H ₃₈ Cl ₅ N ₃ O ₁₁ P ₂ Ru	$C_{50}H_{42}Cl_2N_4O_{10}P_2Ru$	C ₅₁ H ₄₁ Cl ₆ N ₂ O ₃ P ₂ Ru		
formula wt	1197.09	1092.79	1105.57		
space group	$P\overline{1}$	$P\overline{1}$	$Cmc2_1$		
temp (K)	296(2)	296(2)	293(2)		
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73		
cryst syst	triclinic	triclinic	orthorhombic		
a (Å)	12.637(3)	10.9154(7)	14.854(5)		
b (Å)	13.323(3)	13.5046(8)	18.898(5)		
c (Å)	17.448(6)	18.3960(11)	17.153(5)		
α (deg)	102.666(13)	104.619(2)	90.000(5)		
γ (deg)	111.822(9)	90.777(3)	90.000(5)		
β (deg)	98.408(13)	105.312(3)	90.000(5)		
$V(\text{\AA}^3)$	2575.3(13)	2521.4(3)	4815(2)		
Z	2	2	4		
$ ho_{ m calcd} ({ m g \ cm}^{-3})$	1.544	1.439	1.515		
cryst size (mm)	0.25 imes 0.18 imes 0.14	0.32 imes 0.27 imes 0.21	$0.29\times0.23\times0.17$		
F(000)	1212.0	1116.0	2244.0		
θ range for data collection	1.24-28.60	1.19-28.31	1.74-22.06		
index ranges	-16 < h < 16	-14 < h < 14	-15 < h < 15		
	-16 < k < 17	-17 < k < 14	-19 < k < 19		
	-23 < <i>l</i> < 23	-24 < <i>l</i> < 24	-17 < l < 17		
refinement method	full-matrix least squares on F^2				
no. of data/restraints/params	12 486/0/650	11 868/0/625	2954/1/334		
GOF^a on F^2	0.937	1.208	0.945		
$\mathrm{R1}^{b}(I > 2\sigma(I))$	0.0662	0.0587	0.0573		
R1 (all data)	0.0869	0.0865	0.0709		
wR2 ^c $(I > 2\sigma(I))$	0.1872	0.1725	0.1677		
wR2 (all data)	0.2170	0.1994	0.1968		
^{<i>a</i>} GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/M - N]^{1/2}$ $F_c^2)^2]/\Sigma[(F_o^2)^2]]^{1/2}$.	$^{2}(M = \text{number of reflections}, N = \text{number})$	er of parameters refined). ^{<i>b</i>} R1 = $\Sigma F_o - $	$F_{\rm c} /\Sigma F_{\rm o} $. ^c wR2 = $[\Sigma[w(F_{\rm o}^2 -$		

Table 1. Summary of Crystal Data and Data Collection Parameters for 1a · CH₂Cl₂ · 3H₂O, 1b · 2CH₂Cl₂, and 2a · 2H₂O

Table 2.	Selected Bond Lengt	hs (Å)) and	Angles	(deg)	for
1a·CH ₂ CH ₂	$Cl_2 \cdot 3H_2O$, $1b \cdot 2CH_2O$	l ₂ , an	d 2a•	H_2O		

		1a	2a				
Bond Lengths (Å)							
Ru(1)-Cl(1)		2.3503(12)	2.3721(11)				
Ru(1)-P(1)		2.4412(12)	2.4672(12)				
Ru(1)-P(2)		2.4309(13)	2.4529(12)				
Ru(1)-C(37)		2.107(5)	2.071(4)				
Ru(1)-N(1)		2.129(4)	2.094(3)				
Ru(1)-N(2)		1.805(4)					
N(2) - O(1)		1.165(5)	1.160(5)				
Bond Angles (deg)							
O(1)-N(2)-Ru(1)		172.6(4)	170.5(4)				
N(2)-Ru(1)-N(1)		94.15(16)	93.72(15)				
N(2)-Ru(1)-C(37)		171.11(18)	169.31(17)				
N(1)-Ru(1)-C(37)		77.16(17)	75.63(15)				
N(2)-Ru(1)-Cl(1)		101.06(13)	101.30(12)				
N(1)-Ru(1)-Cl(1)		164.73(11)	164.97(10)				
C(37)-Ru(1)-Cl(1)		87.68(14)	89.34(13)				
N(2)-Ru(1)-P(1)		92.86(13)	97.91(12)				
N(1)-Ru(1)-P(1)		95.56(11)	94.04(10)				
C(37)-Ru(1)-P(1)		86.16(12)	83.90(12)				
N(2)-Ru(1)-P(2)	94.25(13)		91.62(12)				
N(1)-Ru(1)-P(2)	92.01(11)		93.18(10)				
C(37)-Ru(1)-P(2)		88.18(12)					
P(1)-Ru(1)-P(2)		169.20(4)	167.63(4)				
Complex 1b							
Bond Lengths (Å)							
Ru(1)-Cl(1)	2.343(4)	Ru(1) - N(1)	2.053(13)				
Ru(1) - P(1)	2.387(2)	Ru(1) - O(1)	2.152(9)				
Ru(1)-C(27)	2.051(14)						
Bond Angles (deg)							
N(1)-Ru(1)-C(27)	77.90(5)	C(27) - Ru(1) - O(1)	155.3(5)				
N(1)-Ru(1)-Cl(1)	179.8(4)	O(1) - Ru(1) - Cl(1)	102.8(3)				

 $\begin{array}{ccccccc} C(27)-Ru(1)-Cl(1) & 101.9(4) & O(1)-Ru(1)-P(1) & 89.07(5) \\ N(1)-Ru(1)-P(1) & 91.24(8) & Cl(1)-Ru(1)-P(1) & 88.77(8) \\ C(27)-Ru(1)-P(1) & 91.46(6) & P(1)-Ru(1)-P(1) & 176.52(15) \\ \end{array}$ Similar to the case for complex $1a \cdot CH_2Cl_2 \cdot 3H_2O$, the $Ru-N_{NO}$ distance (1.805 Å) was found to be longer than the unsated where 1^{4-16} but its out a character to the angles are stable.

 $Ru-N_{NO}$ distance (1.805 Å) was found to be longer than the reported values,^{14–16} but it was closer to the value reported by Crutchley and co-workers.¹⁷ The lengthening of this $Ru-N_{NO}$ bond may be due to the trans effect of the carbanion.¹³

All these data described above clearly indicated the presence of a {RuNO}⁶ moiety (according to Enemark and Feltham notation¹⁸) in both **1a** · CH₂Cl₂ · 3H₂O and **2a** · 2H₂O with an S = 0 ground state. NO stretching frequencies (ν_{NO} at ~1800 cm⁻¹) (vide infra) and N–O bond lengths were consistent with reported values.^{14–19} Ru–N and N–O distances and Ru–N–O angles (172.6° for **1a** · CH₂Cl₂ · 3H₂O and 170.5° for **2a** · 2H₂O) clearly expressed the {Ru^{II}-NO⁺}⁶ description of the {RuNO}⁶ moiety.^{18,19}

[Ru(L^{SB2})(PPh₃)₂Cl] (1b·2CH₂Cl₂). Complex 1b was derived from 1a after photorelease of coordinated NO upon illumination of visible light (vide infra). On examination of the structure derived from crystal structure solution, we found that the only difference between 1 and 1b was the presence of an $-NO_2$ group in the ring containing the phenolato function in the tridentate ligand of complex 1b. Moreover, the bidentate ligands in 1a and 2a retained their tridentate behavior by reestablishing the Ru- O_{Ph} bond. In the molecular structure of $1b \cdot 2CH_2Cl_2$, the carbanion (C(27)), imine nitrogen (N(1)), phenolato oxygen (O_{ph}), and Cl⁻ constituted the equatorial plane, whereas two PPh₃ groups acted as axial ligands. The geometry around the metal center was found to be distorted octahedral. The Ru-C (2.051 Å) distance was consistent with values reported in the literature.^{12,13,17} Ru-N1, Ru-P, and Ru-Cl bond distances were also consistent with the values reported earlier.^{13,20,21}

A comparison of the three structures described above revealed some important points. We have observed that Ru–P distances in $2a \cdot 2H_2O$ and $1a \cdot CH_2Cl_2 \cdot 3H_2O$ were slightly greater than the values reported by Chakravorty and co-workers in the precursor complex¹³ and by Ramesh and co-workers.²⁰ The P–Ru–P angle was found to be 174.4° in $2;^{13}$ however, in the nitrosyl complex $2a \cdot 2H_2O$, this angle was 167.6°. A similar observation was also found in our recent report.⁹ These data indicated greater distortion of axial bonds in the nitrosyl complexes compared to the precursor complexes. A comparison of the P–Ru–P angle in $1a \cdot CH_2Cl_2 \cdot 3H_2O$ and $1b \cdot 2CH_2Cl_2$ also provided similar distortion.

On going from precursor complexes to nitrosyl complexes, it was observed that in nitrosyl complexes there was approximately no change in Ru–Cl bond distance; however, there was a slight increase (0.04–0.08 Å) in Ru–N1, Ru–C,¹⁷ and Ru–P bond lengths. The Ru–O_{Ph} distance was longer than the distances reported in the literature;^{15,21} however, it was consistent with values obtained by Lahiri et al.¹³ and Kannan et al.²⁰ Comparison of these data with literature data predicted that the longer Ru–O_{Ph} bond length was due to the trans effect of the carbanion donor¹³ and this may be important for NO coordination.

Spectroscopic Studies. The electronic spectra of complexes **1a** and **2a** in dichloromethane are displayed in Figure 5. Both complexes exhibited one strong absorption band with λ_{max} near 310 nm. In addition, a strong absorption band with λ_{max} near 412 nm was found in the UV—vis spectrum of complex **2a**, while in the case of **1a** a shoulder was found near 400 nm (Figure 5).

The infrared spectra of both **1a** and **2a** provided an N–O stretching frequency ($\nu_{\rm NO}$) near 1800 cm⁻¹, which was expected for complexes having an {Ru-NO}⁶ moiety.^{14–19} The peaks around 1090 and 623 cm⁻¹ clearly showed the presence of a perchlorate ion⁹ in complexes **1a** and **2a**. The complexes also gave rise to a few new bands in the range 1290–1380 cm⁻¹, which were assigned to probable ring nitration (shown in the Supporting Information). In all of the complexes, the peaks near 745, 695, and 520 cm⁻¹ confirm the presence of PPh₃ groups.²⁰

¹H NMR spectra of **1a** (shown in Figure 4) and **2a** (prepared and run in the dark) clearly indicated the presence of the phenolic O–H proton at 11.75 and 10.35 ppm, respectively, along with other protons present in the complexes. The disappearance of the peak at 11.75 ppm in complex **1a** when the NMR sample solution was shaken with D₂O supported the presence of an exchangeable proton in the –OH functional group (Figure S13, Supporting Information).²² These data supported the dissociation of the Ru–O_{Ph} bond during NO coordination. In both complexes, ³¹P NMR spectra provided a single peak at ~21 ppm, confirming the trans disposition of the PPh₃ groups.²³



Figure 4. ¹H NMR (a) and ³¹P NMR spectra (b) (500 MHz) of complex 1a in (CD₃)₂SO at room temperature.



Figure 5. Electronic absorption spectra of 1a (solid line) and 2a (broken line) in dichloromethane.

In both 1b and 2b, a charge-transfer band near 425 nm was observed. Absorption bands near 528 nm for 1b and 650 nm for 2b were also observed. The infrared spectrum of complex 1b exhibited a band near 1588 cm⁻¹ corresponding to the azomethine ($\nu_{\rm C=N}$) stretching frequency. This band was similar to the band reported by Chakravorty and co-workers.¹² In the infrared spectrum of complex 2b, a few characteristic bands in the range 1400–1500 cm⁻¹ indicated the presence of an azo ($\nu_{\rm N=N}$) stretching frequency.²⁰ In both 1b and 2b, the new bands in the range 1300–1380 cm⁻¹ showed the presence of ring nitration.²¹

Photolysis Experiment of Complex 1a. The dichloromethane solution of complex 1a can be stored in the dark for weeks. However, when such a solution was exposed to visible light (60 W tungsten lamp), a rapid change in color from orange-yellow to red was observed. The photolability of the coordinated NO was examined by illumination of visible light (60 W tungsten lamp) through an acetonitrile solution of complex 1a (shown in Figure 6). No loss of NO was observed when the solution was kept in the dark.

Interestingly, at the end of the photolability experiment of complex 1a (Figure 6), we ended up with the new complex 1b. Spectroscopic characterization and determination of the molecular structure (vide supra) confirmed the formation of 1b



Figure 6. Photodissociation of complex **1a** ($\sim 1.8 \times 10^{-5}$ M) in acetonitrile under illumination with a 60 W tungsten lamp with isosbestic points at 296 and 369 nm. Inset: electronic absorption spectrum of complex **1b** in dichloromethane.

(Figure 3). Therefore, these data prompted us to investigate the flipping of complexes **1a** and **1b** through NO coordination and NO dissociation. Hence, we treated complex **1b** with acidified nitrite solution and isolated complex **1a**. Then we studied the photocleavage of NO from complex **1a** (shown in Scheme 3). These data indicated the dissociation of the phenolato ligand during NO interaction probably due to the trans effect of the carbanion ligand (vide infra). After NO photocleavage, the open position at the metal center became available for the phenolato ligand. Retention of phenolato ligand coordination to the metal center gave rise to the formation of **1b**. Hence, dissociation and re-establishment of Ru–O_{Ph} bond was predicted during NO coordination and photorelease.

It is important to note here that in many cases of ruthenium nitrosyl complex syntheses, the Cl⁻ ligand was substituted by NO,^{3,17} but in this case the Ru–Cl bond was retained. The above findings are indicative of probable participation of a *solvento species* generated due to Ru–O_{Ph} bond dissociation during our reactivity studies.^{22,24} However, we did not observe any appreciable change in UV–vis spectra of 1 and 2 in different solvents (Figures S14 and S15, Supporting Information). Instead of solvent, we tried to provide a negatively charged ligand at the

Scheme 3



metal center to observe $Ru-O_{\rm Ph}$ bond dissociation or Cl^- ligand substitution. We refluxed 1 and 2 with CH₃COONa, NaNO₂, NaN₃, and NaCN in dimethylformamide, and the formation of new ruthenium complexes was indicated. This experiment afforded appreciable changes in UV-vis spectra (Figures S16 and S17, Supporting Information); however, simple stirring with the same reagents described above was not sufficient to cause any change in 1 and 2. Moreover, from the above reactivity studies we cannot predict the dissociation of the Ru-O_{Ph} bond by considering the possibilities of Cl⁻ ligand substitution as well as Ru-O_{Ph} dissociation. Hence, we decided to synthesize 1a from 1b by treating NaNO₂ (under refluxing condition) with 1b followed by acidification. Lahiri and co-workers adopted¹⁶ this procedure for their synthesis of ruthenium nitrosyl complexes, and the Ru-NO₂ moiety was converted to a Ru-NO species under acidic conditions. Synthesis of 1a following the route of Lahiri and co-workers clearly indicated the dissociation of the $Ru-O_{Ph}$ bond, which was responsible for the formation of our nitrosyl complex (details are given in the Supporting Information, Scheme S1). However, the yield was very low in this procedure, and other detailed studies are in progress.

Hence, it is evident from the above data that ligand nitration and nitrosylation at the metal center are the two events happening in this reactivity study. In complex 1, ligand nitration was observed at the para position of the phenolato function. On the other hand, due to the presence of a methyl group at the para position in complex 2, ligand nitration was observed at the position ortho to the phenolato function. This ligand nitration was probably governed by steric factors. We want to mention here that in our recent report⁹ we found oxidative cyclization along with metal nitrosylation and ligand nitration; however, this time we did not observe this cyclization, even though complex 1 belongs to the same family. Work is in progress to get a better insight into the mechanism of oxidative cyclization during this reactivity study.

Photolysis Experiment of Complex 2a. Illumination of visible light through a dichloromethane solution of complex **2a** afforded spectral changes along with isosbestic points at 252, 292, 348, 370, and 438 nm (Figure 7). In this case also we observed a similar type of NO photodissociation and religation of the phenolato oxygen and concomitant formation of **2b**. It is important to note here



Figure 7. Photodissociation of **2a** ($\sim 1.5 \times 10^{-5}$ M) in dichloromethane under illumination with a 60 W tungsten lamp with isosbestic points at 252, 292, 348, 370, and 438 nm. Inset: electronic absorption spectrum of complex **2b** in dichloromethane.

Wavelength (nm)



Figure 8. Electronic spectra of conversion of reduced Mb to Mb–NO adduct upon reaction with **1a** in buffer solution on exposure to the light of a 60 W tungsten lamp: (black line) oxidized Mb (intense band at 409 nm); (red line) reduced Mb (at 434 nm, with excess of sodium dithionite); (green dotted line) reduced Mb + **1a** solution ($\sim 9 \times 10^{-6}$ M) in the dark for 15 min; (blue line) Mb–NO adduct (at 420 nm), obtained by Mb + **1a** solution exposed to 60 W tungsten lamp light for 5 min.

that the rate of photodissociation of complex 2a was higher than that of 1a. This may be due to the presence of a higher absorbance of 2a in the visible region compared to 1a (Figure 5 and Figure S12 (Supporting Information)).¹⁵

Transfer of NO to Myoglobin. The photocleavage of the coordinated NO was also confirmed by trapping the liberated NO by reduced myoglobin (shown in Figure 8). Electronic absorption spectra were obtained in phosphate buffer (6.8 pH). The UV-vis spectrum of oxidized myoglobin (Mb) showed an intense band at 409 nm (Soret band). The UV-vis spectrum of reduced myoglobin at 434 nm was obtained by addition of excess sodium dithionite to the same cuvette. When an acetonitrile solution of complex 1a was added to a buffer solution of reduced myoglobin under dark conditions, no reaction was observed. However, when the same mixture was exposed to a tungsten lamp (60 W) for 5 min, its absorption spectrum at 420 nm showed the formation of an Mb-NO adduct.^{14,25} We have also trapped the photocleaved NO derived from complex 2a by reduced myoglobin, and the results are deposited in the Supporting Information (Figure S11).

2503

CONCLUSION

In conclusion, we have prepared two different σ -aryl nitrosyl ruthenium complexes: [Ru(L^{SB2}H)(PPh₃)₂(NO)Cl]ClO₄ (1a) and $[Ru(L^{AZ2}\hat{H})(PPh_3)_2(NO)CI](ClO_4)$ (2a). The molecular structures of both complexes were determined by X-ray crystallography. These novel ruthenium cyclometalates were characterized by ¹H and ³¹P NMR spectral studies, because the complexes were diamagnetic with an S = 0 ground state of the metal center. Ru-N and N-O distances and the Ru-N-O angle from the crystallographic data along with the NO stretching frequency $(\nu_{\rm NO})$ clearly indicated the presence of {RuNO}⁶ moiety with a {Ru^{II}NO⁺}⁶ description. Ligand nitration was observed in the ring bearing the phenolato function. The coordinated NO was found to be photolabile under visible light. The rate of photodissociation of complex 2a was higher than that of 1a. The photoreleased NO was trapped by reduced myoglobin. Interestingly, we found out that complexes 1a and 2a gave rise to complexes 1b and 2b, respectively, after photorelease of NO and 1a and 2a could be regenerated by treating 1b and 2b with acid nitrite solution. Hence, the meridional tridentate ligand became bidentate during NO coordination and after photocleavage of NO the ligand retained its tridentate properties. These data clearly showed the reversible binding of the phenolato function to the metal center during photorelease and coordination of NO at the metal center. To the best of our knowledge, this is the first example of such types of organometallic NO donors. Modification of the ligand and biological application of these novel complexes are in progress.

EXPERIMENTAL SECTION

Materials. All the solvents used were reagent grade. The analytical grade reagents sodium nitrite (Sigma Aldrich, Steinheim, Germany), $RuCl_3 \cdot 3H_2O$ and triphenylphosphine (SRL, Mumbai, India), 2-aminophenol, 2-amino-4-methylphenol, 4-chlorobenzaldehyde, *p*-toluidine, and sodium perchlorate hydrate (Himedia Laboratories Pvt. Ltd., Mumbai, India), disodium hydrogen phosphate anhydrous (RFCL Ltd., New Delhi, India), and sodium dihydrogen phosphate (Chemport India Pvt. Ltd. Mumbai, India) were used as obtained. Double-distilled water was used in all the experiments. Equine skeletal muscle myoglobin was obtained from Sigma Aldrich, Steinheim, Germany.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with caution.

Preparation of Complexes. Synthesis of $[Ru(L^{SB1})(PPh_3)_2CI]$ (1). $[Ru(L^{SB1})(PPh_3)_2CI]$ (1) was synthesized from the reaction of $[Ru(PPh_3)_3Cl_2]$ with the ligand $L^{SB1}H_2$ (where $L^{SB1}H_2 = 2$ -(4-chloroben-zylideneamino)phenol and H = dissociable protons) in ethanol according to the method reported earlier.¹²

Synthesis of [**Ru**(L^{SB2} **H**)(**PPh**₃)₂(**NO**)**Cl**]**ClO**₄ (**1a**). A portion of complex 1 (0.03 g, 0.033 mmol) was dissolved in 30 mL of dichloromethane in a 100 mL round-bottom flask to give a purple solution. To the above solution was added sodium nitrite (0.3 g, 4.5 mmol) with acidified distilled water (20 mL), and the mixture was stirred at room temperature for 1 h to give a yellowish orange solution of complex 1a. The dichloromethane layer was separated out, and NaClO₄ (in excess) with 5 mL of methanol was added to this solution. Stirring of this solution was continued for another 1 h. The solvent was evaporated to give an orange solid. To remove the excess NaClO₄, the compound was further dissolved in dichloromethane and this solution was filtered out. Complex 1a (0.018 g, 0.017 mmol) was eluted from an alumina column with a dichloromethane/ methanol (9/1) mixture. Single crystals of the complex for X-ray crystallography were obtained within 2 days upon slow evaporation of the dichloromethane/methanol mixture. Yield: 52%. IR (KBr disk, cm⁻¹): 1803 (ν_{NO}), 1578 ($\nu_{C=N}$), 1383, 1345, 1300 (ν_{NO_2}), 1089, 623 (ν_{CIO_4}), 745, 696, 521 (ν_{PPh_3}) cm⁻¹. UV–vis (CH₃CN; λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)): 235 (41 389), 312 (33 445), 392 (4889). ³¹P NMR ((CD₃)₂SO, 500 MHz): δ 20.92 ppm. ¹H NMR ((CD₃)₂SO, 500 MHz): δ 11.75 (s, 1H), 8.743 (s, 1H), 8.027 (d, 1H), 7.702 (d, 1H), 7.472–7.159 (m, 31H), 6.923 (d, 1H), 6.812 (s, 1H), 6.338 (s, 1H).

Interconversion of Complexes [Ru(L^{SB2}H)(PPh₃)₂(NO)CI]ClO₄ (1a) and [Ru(L^{SB2})(PPh₃)₂CI] (1b). (*i*) Conversion of Complex 1a into 1b. A yellowish orange dichloromethane solution of complex 1a (0.02 g, 0.019 mmol) was exposed to the light of a tungsten lamp (60 W). Within 0.5 h the solution turned from yellow to red. The solvent was evaporated to obtain a red-orange solid, and this was washed thoroughly with methanol and ether. Complex 1b was eluted on an alumina column with a dichloromethane/hexane (1/1) mixture. Single crystals of 1b·2CH₂Cl₂ for X-ray crystallography were obtained within 3 days by slow diffusion of hexane into a solution of the complex in dichloromethane (0.012 g, 0.013 mmol). Yield: 68%. IR (KBr disk, cm⁻¹): 1630, 1588 ($\nu_{C=N}$), 1382, 1340 (ν_{NO_2}), 1297, 1092, 744, 695, 523 (ν_{PPh_3}) cm⁻¹. UV–vis (CH₂Cl₂; λ_{max} nm (ϵ , M⁻¹ cm⁻¹)): 431 (6329), 528 (2359).

(ii) Conversion of Complex **1b** into **1a**. A portion of complex **1b** (0.028 g, 0.03 mmol) was dissolved in 25 mL of dichloromethane in a 100 mL round-bottom flask to give a red solution. Then 20 mL of acidified distilled water was layered over this solution. Sodium nitrite (0.2 g, 3 mmol) was added to the bilayer solution, and the mixture was stirred at room temperature for 45 min to give a yellowish orange solution of complex **1a**. The dichloromethane layer was separated out, and NaClO₄ (in excess) with 5 mL of methanol was added to this solution. Stirring of this solution was continued for another 1 h. The solvent was evaporated to give an orange solid of complex **1a** (0.015 g, 0.014 mmol). Yield: 47%.

Synthesis of [Ru(L^{AZ1})(PPh₃)₂Cl] (2). Complex [Ru(L^{AZ1})-(PPh₃)₂Cl] (2) was synthesized from the reaction of [Ru(PPh₃)₃Cl₂] with the ligand $L^{AZ1}H_2$ (where $L^{AZ1}H_2 = 4$ -methyl-2-(*p*-tolyldiazenyl)-phenol and H = dissociable protons) in ethanol by following the method reported earlier.¹³

Synthesis of [Ru(L^{AZ2}H)(PPh₃)₂(NO)Cl]ClO₄ (2a). Complex 2a was synthesized using 2 by following the same procedure as for 1a. Yield: 48%. IR (KBr disk, cm⁻¹): 1805 (ν_{NO}), 1623, 1577, 1540, 1479, 1434 ($\nu_{N=N}$), 1345, 1305 (ν_{NO_2}), 1254, 1090, 623 (ν_{ClO_4}), 748, 692, 517 (ν_{PPh_3}). UV–vis (CH₂Cl₂; λ_{max} , nm (ε , M⁻¹ cm⁻¹)): 231 (49 067), 312 (30 667), 408 (12 000). ¹H NMR (CDCl₃, 500 MHz): δ 10.35 (s, 1H), 8.291 (d, 1H), 7.932 (s, 1H), 7.454–7.175 (m, 31H), 6.825 (s, 1H), 6.084 (s, 1H), 2.187 (s, 3H), 1.813 (s, 3H). ³¹P NMR (CDCl₃, 500 MHz): δ 21.87 ppm.

Interconversion of Complexes [Ru(L^{AZ2} H)(PPh₃)₂(NO)CI]ClO₄ (2a) and [Ru(L^{AZ2})(PPh₃)₂CI] (2b). (*i*) Conversion of Complex **2a** into **2b**. A yellowish-orange dichloromethane solution (20 mL) of complex **2a** (0.03 g, 0.028 mmol) was exposed to the light of a tungsten lamp (60 W). Within 15 min the solution turned from yellow to light green. The solvent was evaporated, and the residue was washed thoroughly with methanol and ether to obtain a green solid of complex **2b** (0.018 g, 0.019 mmol). Yield: 67.86%. IR (KBr disk, cm⁻¹): 1614, 1571, 1547, 1510, 1481, 1434 ($\nu_{N=N}$), 1348, 1301 (ν_{NO_2}), 1256, 1225, 1092, 745, 694, 517 (ν_{PPh_3}) cm⁻¹. UV-vis (CH₂Cl₂; λ_{max} , nm (ε , M⁻¹ cm⁻¹)): 270 (25 208), 440 (6042), 650 (4042).

(ii) Conversion of Complex **2b** into **2a**. A portion of complex **2b** (0.025 g, 0.027 mmol) was dissolved in 20 mL of dichloromethane in a 100 mL round-bottom flask to give a light green solution. Then 25 mL of acidified distilled water was layered over this solution. Sodium nitrite (0.2 g, 3 mmol) was added to the bilayer solution, and the mixture was stirred at room temperature for 45 min to give a yellowish orange

solution of complex 2a. The dichloromethane layer was separated out, and NaClO₄ (in excess) with 5 mL of methanol was added to this solution. Stirring of this solution was continued for another 1 h. The solvent was evaporated to give an orange solid of complex 2a (0.012 g, 0.011 mmol). Yield: 40.7%.

Physical Measurements. Infrared spectra were obtained as KBr pellets with a Thermo Nikolet Nexus FT-IR spectrometer, using 16 scans, and are reported in cm⁻¹. Electronic absorption spectra were recorded in dichloromethane and acetonitrile solvents with a Thermo Scientific Evolution 600 UV–vis spectrophotometer. ¹H and ³¹P NMR spectra were recorded on a Bruker AVANCE 500.13 MHz spectrometer in deuterated solvents.

X-ray Crystallography. Orange-red crystals of $1a \cdot CH_2Cl_2 \cdot 3H_2O$ and $2a \cdot 2H_2O$ were obtained by slow evaporation of solutions of the complexes in CH_2Cl_2 /methanol. The crystal structures showed the presence of water molecules in the lattice. Crystals of $1b \cdot 2CH_2Cl_2$ were obtained by slow diffusion of hexane into the solution of complex 1b in dichloromethane. The X-ray data collection and processing for the complexes were performed on a Bruker Kappa Apex-II CCD diffractometer by using graphite-monochromated Mo K α radiation ($\lambda =$ 0.71070 Å) at 296 K for $1a \cdot 2CH_2Cl_2$ and $2a \cdot 2H_2O$ and at 293 K for $1b \cdot CH_2Cl_2 \cdot 3H_2O$. Crystal structures were solved by direct methods. Structure solutions, refinement, and data output were carried out with the SHELXTL program.^{26,27} All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. Images were created with the DIAMOND program.²⁸

ASSOCIATED CONTENT

Supporting Information. Figures giving characterization data of complexes by IR and NMR spectral studies and electronic absorption spectra of NO transfer to myoglobin of complexes **1a** · CH₂Cl₂ · 3H₂O, **2a** · 2H₂O, and **1b** · 2CH₂Cl₂. This material is available free of charge via the Internet at http://pubs.acs.org.

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DEDICATION

[†]Dedicated to Prof. Animesh Chakravorty on his 75th birthday.

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