Ruthenium complexes containing 2-(2-nitrosoaryl)pyridine : structural, spectroscopic and theoretical studies

Chan, Siu-Chung; Cheung, Ho-Yuen; Wong, Chun-Yuen

2011

Chan, S.-C., Cheung, H.-Y. & Wong, C.-Y. (2011). Ruthenium complexes containing 2-(2-nitrosoaryl)pyridine : structural, spectroscopic and theoretical studies. *Inorganic chemistry*, 50(22), 11636-11643.

<https://hdl.handle.net/10356/107440>

<https://doi.org/10.1021/ic201570d>

© 2011 American Chemical Society. This is the author created version of a work that has been peer reviewed and accepted for publication by *Inorganic Chemistry*, American Chemical Society. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1021/ic201570d>].

Downloaded on 26 Apr 2023 23:22:20 SGT

Ruthenium Complexes Containing 2-(2-Nitrosoaryl)pyridine: Structural, Spectroscopic, and Theoretical Studies

*Siu-Chung Chan, Ho-Yuen Cheung, and Chun-Yuen Wong**

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon,
Hong Kong SAR, People's Republic of China

acywong@cityu.edu.hk

ABSTRACT. Ruthenium complexes containing 2-(2-nitrosoaryl)pyridine ($\text{ON}^{\wedge}\text{N}$) and tetradentate thioether 1,4,8,11-tetrathiacyclotetradecane ($[\text{14}]_{\text{aneS4}}$), $[\text{Ru}(\text{ON}^{\wedge}\text{N})([\text{14}]_{\text{aneS4}})]^{2+}$ (**2a–2d**; $\text{ON}^{\wedge}\text{N}$ = 2-(2-nitrosophenyl)pyridine (**a**), 10-nitroso-benzo[h]quinoline (**b**), 2-(2-nitroso-4-methylphenyl)pyridine, (**c**), 2-(2-nitrosophenyl)-5-(trifluoromethyl)pyridine (**d**)), and analogues with the 1,4,7-trithiacyclononane ($[\text{9}]_{\text{aneS3}}$)/tert-butyliisocyanide ligand set, $[\text{Ru}(\text{ON}^{\wedge}\text{N})([\text{9}]_{\text{aneS3}})(\text{C}\equiv\text{N}^t\text{Bu})]^{2+}$ (**4a**, **4b**) have been prepared by insertion of nitrosonium ion (NO^+) into the Ru–aryl bond of cyclometallated Ru(II) complexes. The molecular structures of the $\text{ON}^{\wedge}\text{N}$ –ligated complexes **2a** and **2b** reveal that (i) the $\text{ON}^{\wedge}\text{N}$ ligands behave as bidentate chelates via the two N atoms and the bite angles are 86.84(18)–87.83(16)°; (ii) the Ru–N_{NO} and N–O distances are 1.942(5)–1.948(4) and 1.235(6)–1.244(5) Å respectively. The Ru–N_{NO} and N–O distances, together with the $\nu_{\text{N=O}}$, suggest that the coordinated $\text{ON}^{\wedge}\text{N}$ ligands in this work are neutral moiety (ArNO)⁰ rather than monoanionic radical (ArNO)^{•1–} or dianion (ArNO)^{2–} species. The nitrosated complexes **2a–2d** show moderately intense absorption centered at 463–484 nm ($\epsilon_{\text{max}} = (5\text{--}6) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and a clearly discriminable absorption

shoulder around 620 nm ($\epsilon_{\text{max}} = 6 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) which tails up to 800 nm. These visible absorptions are assigned as a mixing of d(Ru) $\rightarrow$ ON[^]N metal-to-ligand charge transfer (MLCT) and ON[^]N intra-ligand (IL) transitions on the basis of time-dependent density functional theory (TD-DFT) calculations. The first reduction couples of the nitrosated complexes range from -0.53 to -0.62 V vs. $\text{Cp}_2\text{Fe}^{+/0}$, which are 1.1–1.2 V less negative than that for $[\text{Ru}(\text{bpy})([\text{14}] \text{aneS4})]^{2+}$ (bpy = 2,2'-bipyridine). Both electrochemical data and DFT calculations suggest that the lowest-unoccupied molecular orbitals (LUMOs) of the nitrosated complexes are ON[^]N-centered. Natural population analysis (NPA) shows that the amount of positive charge on the Ru centers and the $[\text{Ru}([\text{14}] \text{aneS4})]$ moieties in **2a** and **2b** are larger than that in $[\text{Ru}(\text{bpy})([\text{14}] \text{aneS4})]^{2+}$. According to the results of the structural, spectroscopic, electrochemical and theoretical investigations, the ON[^]N ligands in this work have considerable π -acidic character and behave as better electron acceptors than bpy.

Introduction

The coordination chemistry of *C*-nitroso compounds ($\text{RN}=\text{O}$, R = alkyl or aryl) is of considerable interest from several perspectives. In the context of organic synthesis, *C*-nitroso compounds are attractive electrophiles in many carbon–nitrogen and/or carbon–oxygen bond forming reactions,¹⁻⁹ and the investigations on the *C*-nitroso metal complexes provided useful results for the development of metal-mediated organic transformation reactions. Besides, the ability of nitrosoarenes to bind to the heme proteins like hemoglobin and myoglobin revealed their importance in various metabolic processes,¹⁰⁻¹⁴ and this initiated a lot of studies on the electronic structures of metal–nitrosoarene complexes.¹⁵⁻²³ Importantly, nitrosoarene ligands are redox-active,²⁴⁻²⁷ and understanding the chemistry of metal–nitrosoarene complexes can bring fundamental advances in inorganic and biological chemistry, although it has been recently pointed out by Wieghardt and co-workers that such rich redox activity has been largely overlooked in the literature.²⁸

Our interest in the coordination chemistry of *C*-nitroso compounds stems from our recent discovery that nitrosonium ion (NO^+) inserts into the Ru–aryl bond of 2-phenylpyridine anion (PhPy)-ligated

Ru(II) complexes $[\text{Ru}(\text{PhPy})([9]\text{aneS3})(\text{L})]^+$ ($[9]\text{aneS3}$ = 1,4,7-trithiacyclononane) to give 2-(2-nitrosophenyl)pyridine (NO-PhPy)-coordinated $[\text{Ru}(\text{NO-PhPy})([9]\text{aneS3})(\text{L})]^{2+}$.²⁹ These NO-PhPy-ligated complexes represent the first structurally characterized transition metal complexes bearing nitrosoarene with pyridyl chelate, for which the NO-PhPy behaves as a bidentate ligand via the two N atoms, with the bite angle close to 90°. Interestingly, the dihedral angles for the Ph/C–N–O plane pair and the Ph/Py pair in the crystal structure of $[\text{Ru}(\text{NO-PhPy})([9]\text{aneS3})(\text{CH}_3\text{CN})]^{2+}$ are 36° and 26° respectively, indicating that the pyridyl, phenyl, and NO moieties should in principle allow certain degree of electron delocalization. We envision that comparing the structural, electrochemical, and spectroscopic properties of transition metal complexes bearing 2-(2-nitrosoaryl)pyridine (denoted as ON[^]N) with their corresponding aromatic diimine analogues (like bpy-ligated complexes) may yield interesting and important information regarding the metal–(ON[^]N) bonding interaction in both the ground and the excited states. We now present the preparation, structural, electrochemical, spectroscopic and theoretical investigations of two series of Ru complexes containing ON[^]N and multidentate thioether ligands $[9]\text{aneS3}$ or 1,4,8,11-tetrathiacyclotetradecane ($[14]\text{aneS4}$). Our results suggest that the coordinated nitrosoarene on ON[^]N should be regarded as a neutral π -acid moiety (ArNO)⁰ rather than monoanionic radical (ArNO)^{•1-} or diamagnetic dianion (ArNO)²⁻, and the ON[^]N are better electron acceptors than aromatic diimines.

RESULT AND DISCUSSION

Synthesis and Characterization. Nitroso complexes $[\text{Ru}(\text{ON}^{\wedge}\text{N})([14]\text{aneS4})]^{2+}$ (**2a–2d**) have been prepared in 60–80% yields by reacting the cyclometalated complexes **1a–1d** with $[\text{NO}][\text{BF}_4]$ (Scheme 1). The reaction proceeds smoothly to completion within 1 min at room temperature. This reactivity is the same as our recently reported insertion reaction of NO^+ into the Ru–C bond of the cyclometalated Ru(II) complex **3a** to give ON[^]N-ligated complex **4a**.²⁹ This is different from that for many Ru(II) complexes which react with NO^+ substitutionally to give the ligand-substituted Ru–nitrosyl compounds.^{30–34} The $[9]\text{aneS3}$ -isocyanide-ligated complexes **4a** and **4b** have also been prepared to compare the electron donating/accepting ability of the ON[^]N ligands with aromatic diimines as the $\nu_{\text{C}\equiv\text{N}}$

value for $[\text{Ru}([\text{9}]ane\text{S}3)(\text{phen})(\text{C}\equiv\text{N}^t\text{Bu})]^{2+}$ is available in the literature (2167 cm^{-1}).³⁵ The $\nu_{\text{C}\equiv\text{N}}$ values for complexes **4a** and **4b** (2188 and 2185 cm^{-1} respectively) are larger than that for the phen-ligated analogues by ca. 20 cm^{-1} , revealing that the ON[^]N ligands are better electron acceptor than simple aromatic diimines. All the ON[^]N-ligated complexes in this work have been found to be diamagnetic at room temperature, and the ν_{NO} values range from $1365\text{--}1396\text{ cm}^{-1}$. These findings, together with the Ru–N_{NO} and N–O distances of **2a** and **2b** (see discussion below) suggest that the ON[^]N ligands in this work should be assigned as neutral (ArNO)⁰ ligands rather than monoanionic radical (ArNO)^{•1-} or diamagnetic dianion (ArNO)²⁻ species.

Scheme 1.

The crystal structures of complexes **1a**, **2a**, and **2b** have been determined by X-ray crystallography. Perspective views of their cations are depicted in Figure 1. Selected bond distances and angles are summarized in Table 1. In each case, the Ru atom adopts a *cis*-octahedral geometry. Disorder have been observed in the [14]aneS4 ligands for the cations in **2a** and **2b**, which are attributed to there being two possible ways that a [14]aneS4 coordinates to a *cis*-[Ru(X)(Y)] moiety (Scheme 2a). Although three possible isomers can arise from the orientation of the lone pairs of the equatorial S atoms (Scheme 2b),³⁶ only ligand conformation **II** has been observed crystallographically in the complexes in this work.

Figure 1. Perspective views of the cations in **1a**(ClO₄), **2a**(ClO₄)₂, and **2b**(PF₆)₂•CH₃NO₂. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are at the 30% probability level.

Scheme 2. (a) Two possible ways that a [14]aneS4 coordinates to a *cis*-[Ru(X)(Y)] moiety. (b) Three possible isomers arise from the orientation of the lone pairs of the equatorial S atoms.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1a**(ClO₄), **2a**(ClO₄)₂, and **2b**(PF₆)₂•CH₃NO₂

	1a (ClO ₄)	2a (ClO ₄) ₂ ^a	2b (PF ₆) ₂ •CH ₃ NO ₂
Ru–N _{NO}		1.948(4), 1.942(5)	1.9435(19)
Ru–N _{Py}	2.121(7)	2.141(4), 2.137(4)	2.1115(19)
N _{NO} –O		1.244(5), 1.235(6)	1.242(3)
Ru–C	2.077(9)		
N _{NO} –C		1.428(7), 1.442(7)	1.445(3)
Ru–S(<i>trans</i> to NO)		2.3928(12), 2.42 ^d	2.40 ^d
Ru–S(<i>trans</i> to Py)		2.3140(13), 2.3104(12)	2.33 ^d
Ru–N–O		125.5(3), 126.9(4)	125.13(17)
Ru–N _{NO} –C		119.9(3), 119.9(4)	120.29(16)
O–N _{NO} –C		114.4(4), 113.1(5)	114.3(2)
N _{NO} –Ru–N _{Py}		87.83(16), 86.84(18)	87.19(8)
∠ Py/Ar ^b	7.36	32.91, 25.58	15.52
∠ Ar/C–N–O ^c		36.83, 36.37	27.22

^aThe crystal contains two crystallographically independent Ru complexes in the asymmetric unit. ^bThe angle between the mean plane of the pyridyl ring and the cyclometalated aryl ring (for **1a**) or the nitrosated aryl ring (for **2a** and **2b**). ^cThe angle between the mean plane of the nitrosated aryl ring and the plane constructed by the C, N, O atoms. ^dThe S atoms are disordered over two positions, and the Ru–S bond distances are weighted by the occupancy factors.

In the ON[^]N-ligated complexes, the ON[^]N ligands behave as bidentate chelates via the two N atoms. The [Ru–NO–C] moieties are essentially planar with the sum of the angles around the N_{NO} ranging from 359.7–360.0°, consistent with sp² hybridization at the N_{NO} atoms. The Ru–N_{NO} distances (1.942(5)–1.948(4) Å) are appreciably shorter than the Ru–N_{Py} distances (2.1115(19)–2.141(4) Å), suggesting that the Ru → N_{NO} backbonding interaction is stronger than that for Ru → N_{Py}. On the other hand, the nitrosated aryl rings have a stronger *trans* influence than pyridyl ring: the Ru–S(*trans* to NO) and Ru–S(*trans* to Py) are 2.39–2.42 and 2.31–2.33 Å, respectively. The N_{NO}–O bond distances range from 1.235(6)–1.244(5) Å, which is indicative of N–O double bond character. These values are also

comparable to other literature reported Ru(II) complexes with nitrosoarene.^{22,37} It is known that nitrosoarene may coordinate to a metal center as a neutral (ArNO)⁰ ligand, monoanionic radical (ArNO)^{•1-}, or diamagnetic dianion (ArNO)²⁻.²⁸ On the basis of the Ru–N_{NO} and N–O distances, the coordinated nitrosoarene in the ON^N in this work should be assigned as a neutral species.

The bite angles for the ON^N are 86.84(18)–87.83(16)°, which are comparable to that in [Ru(NO-PhPy)([9]aneS3)(CH₃CN)]²⁺ (87.27(8)°).²⁹ It is also noted that the dihedral angles for the aryl/C–N–O plane pair and the aryl/Py pair are 27.2–36.8° and 15.5–32.9° respectively, suggesting that the electronic delocalization over the whole ON^N unit is possible. This is also supported by DFT calculations (see discussion below).

UV–Visible Absorption Studies. The UV–visible spectral data of all the complexes are summarized in Table 2, and the absorption spectra of selected complexes are depicted in Figure 2. All complexes exhibit intense absorption at $\lambda_{\text{max}} \leq 300$ nm ($\epsilon_{\text{max}} \geq 10^4$ dm³ mol⁻¹ cm⁻¹). Cyclometalated complexes **1a–1d** display moderately intense absorption centered at 384–416 nm ($\epsilon_{\text{max}} = (4–6) \times 10^3$ dm³ mol⁻¹ cm⁻¹), whereas nitrosated complexes **2a–2d** show moderately intense absorption centered at 463–484 nm ($\epsilon_{\text{max}} = (5–6) \times 10^3$ dm³ mol⁻¹ cm⁻¹) and a clearly discriminable absorption shoulder around 620 nm ($\epsilon_{\text{max}} = 6 \times 10^2$ dm³ mol⁻¹ cm⁻¹) which tails up to 800 nm. Although the impact of the substituent on the pyridyl and the nitrosated phenyl rings upon the absorption bands in the visible region is not dramatic, the absorption bands should contain some Ru(II) → ON^N metal-to-ligand charge transfer (MLCT) character because the peak maximum red-shifts in energy as the metal core changes from [Ru([9]aneS3)(C≡N^tBu)] to [Ru([14]aneS4)] (442 nm for **4a**, 463 nm for **2a**), and as the conjugation of the ON^N increases (463 nm for **2a**, 484 nm for **2b**; 442 nm for **4a**, 460 nm for **4b**). In line with this argument, TD-DFT calculations suggest the visible absorption for **2a** and **2b** to be a mixing of d(Ru) → ON^N MLCT and ON^N intra-ligand (IL) transitions (see discussion below).

Figure 2. UV–visible absorption spectra of **1a**, **2a**, **2b**, **4a** and $[\text{Ru}([14]\text{aneS4})(\text{bpy})]^{2+}$ in CH_3CN at 298 K.

It is noted that the $\text{Ru(II)} \rightarrow \text{ON}^{\wedge}\text{N}$ MLCT transition energies are red-shifted by at least 3000 cm^{-1} compared with that for the $\text{Ru(II)} \rightarrow \text{bpy}$ MLCT transition in $[\text{Ru}(\text{bpy})([14]\text{aneS4})]^{2+}$ ($\lambda_{\text{max}} = 401\text{ nm}$). Similar finding has also been observed when comparing the MLCT transition energies for **4a** and **4b** with their aromatic diimine analogue ($[\text{Ru}(\text{phen})([9]\text{aneS3})(\text{C}\equiv\text{N}^t\text{Bu})]^{2+}$ ($\lambda_{\text{max}} = 388\text{ nm}$). All these results suggest that the $\text{ON}^{\wedge}\text{N}$ ligand, even not in a perfectly coplanar configuration, feature a lower-energy π^* molecular orbital than the nearly coplanar aromatic diimines. This is likely attributed to the involvement of the low-lying π^* of the $[\text{N}=\text{O}]$ moiety in the π system of the $\text{ON}^{\wedge}\text{N}$ ligands.

Table 2. UV–Visible Absorption Data^a

complex	λ_{max} / nm (ϵ / $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)
1a	253 (18570), 284 (19180), 384 (5390)
1b	258 (30480), 303 (sh, 7060), 349 (6270), 397 (5410)
1c	254 (19220), 284 (22850), 378 (6060)
1d	258 (15200), 297 (17160), 350 (sh, 2690), 416 (4710)
2a	238 (24970), 289 (13440), 320 (sh, 7330), 463 (5860), 610 (sh, 570)
2b	266 (23800), 325 (10170), 484 (5610), 612 (sh, 980)
2c	238 (sh, 25340), 258 (sh, 19590), 295 (16460), 416 (sh, 4070), 470 (6130), 612 (sh, 630)
2d	236 (sh, 25690), 267 (15400), 294 (sh, 12640), 326 (sh, 8700), 468 (5800), 618 (sh, 620)
3a	244 (19220), 277 (17630), 332 (sh, 3900), 380 (2450)
3b	255 (34330), 286 (sh, 9870), 337 (8200), 404 (2820)
4a	232 (sh, 16660), 253 (13790), 285 (12820), 390 (sh, 2970), 442 (4520)
4b	262 (31530), 320 (13710), 391 (4120), 460 (6670), 510 (sh, 4640)
[Ru(bpy)([14]aneS4)](PF ₆) ₂	243 (9080), 279 (19830), 299 (sh, 10010), 317 (7720), 401 (3770)

^aSolvent = CH₃CN; temperature = 298 K.

Cyclic Voltammetry. Cyclic voltammetry has been used to examine the electrochemistry of all the complexes in this work (Table 3; all values vs. Cp₂Fe⁺⁰). No oxidation wave has been observed for the nitrosated complexes **2a–2d**, **4a** and **4b** within the solvent window (solvent = CH₃CN), and their first reduction couples range from –0.53 to –0.62 V. Since the first reduction couples are sensitive to the change of substituents on both the pyridyl and the nitrosated aryl rings of the ON^N ligands, the lowest-unoccupied molecular orbitals (LUMOs) of the nitrosated complexes may contain a contribution from the ON^N ligand. This is in agreement with our DFT calculations that the lowest-unoccupied molecular orbitals (LUMOs) of these complexes are ON^N-centered (see discussion below). It is noted that the first reduction potentials for **2a–2d** are 1.1–1.2 V less negative than that for [Ru(bpy)([14]aneS4)]²⁺ (–

1.72 V), and this is well-predicted by DFT calculations: the energies of the LUMOs of **2a** and **2b** are calculated to be 1 eV lower than that of [Ru(bpy)([14]aneS4)]²⁺. For the cyclometalated complexes, the $E_{1/2}$ values for the first oxidation couples are 0.40–0.57 V for the [14]aneS4-ligated **1a–1d**, which are less positive than those for the [9]aneS3-isocyanide-supported counterparts (0.67–0.68 V for **3a–3b**).

Table 3. Electrochemical Data^a

complex	$E_{1/2}^b$ / V vs Cp ₂ Fe ⁺⁰		
	Oxidation	First Reduction	Second Reduction
1a	0.40		
1b	0.43	−2.40 ^c	
1c	0.40		
1d	0.49	−2.31 ^c	
2a		−0.61	−1.66
2b		−0.62	−1.48
2c		−0.62	−1.63 ^c
2d		−0.53	−1.49
3a	0.68		
3b	0.67	−2.36 ^c	
4a		−0.62	−1.63
4b		−0.59	−1.57
[Ru([14]aneS4)(bpy)] ²⁺	1.13	−1.72	

^aSupporting electrolyte: 0.1 M [Bu₄N]PF₆ in CH₃CN. ^b $E_{1/2} = (E_{pc} + E_{pa})/2$ at 298 K for reversible couples. ^cIrreversible; the recorded potential is the cathodic potential at scan rate of 100 mV s^{−1}.

Theoretical Calculations. Density functional theory (DFT) calculations have been performed on **2a**, **2b**, and $[\text{Ru}(\text{bpy})([14]\text{aneS4})]^{2+}$. The ground-state, gas-phase structures of these complexes have been optimized at the DFT level (B3LYP).^{38,39} The ECP28MDF pseudopotential has been employed for the Ru atoms with the correlation consistent cc-pVTZ-PP basis set of Peterson *et al.*,⁴⁰ and the 6-31+G* basis set for C, H, N, O, and S atoms.⁴¹ The optimized structures have been confirmed to be local minima by frequency calculations. Detailed optimized structural data are summarized in Supporting Information. The DFT-optimized structures for the calculated complexes are similar to their experimental structures. For example, the calculated Ru–N_{NO}, N–O bond distances, and the bite angles of the ON[^]N are 1.97 Å, 1.24 Å and 87° for **2a** and **2b**, which are comparable to their experimental values (1.942(5)–1.948(4) Å, 1.235(6)–1.244(5) Å, and 86.27(12)–87.83(16)° respectively). Figure 4 depicts the optimized structures and the frontier molecular orbitals (MOs) surfaces of **2a** and **2b**. Table 4 summarizes the compositions of the MOs which are of spectroscopic importance (see discussion below). Although both the highest-occupied molecular orbitals (HOMOs) and lowest-unoccupied molecular orbitals (LUMOs) of **2a** and **2b** are delocalized on the whole complexes, the HOMOs contains more d(Ru) character than the LUMOs, and the LUMOs are dominated by the ON[^]N (ca. 60%).

Figure 4. Optimized structures for **2a** and **2b** and their frontier molecular orbital surfaces (surface isovalue = 0.06 au) from TD-DFT calculations (gas phase).

Table 4. Molecular Orbital Compositions (%) of **2a** and **2b** in gas phase and CH₃CN at the DFT-B3LYP-optimized Geometry

complex	MO	s,p(Ru)	d(Ru)	ON ^N	[14]aneS4
2a (gas phase)	HOMO	2.17	25.68	49.46	22.69
	LUMO	22.47	3.03	59.18	15.31
2b (gas phase)	HOMO	6.66	17.58	50.68	25.07
	LUMO	18.61	3.29	61.79	16.31
2a (CH ₃ CN)	HOMO-5	9.30	2.32	75.59	12.79
	HOMO-4	37.00	1.06	53.77	8.16
	HOMO-3	18.43	14.41	50.43	16.72
	HOMO-2	3.43	24.29	60.82	11.47
	HOMO-1	17.28	32.79	15.27	34.65
	HOMO	2.98	25.37	51.15	20.48
	LUMO	18.15	3.24	61.31	17.29
2b (CH ₃ CN)	HOMO-5	34.06	5.74	50.97	9.22
	HOMO-4	19.53	5.22	51.16	24.07
	HOMO-3	25.13	19.45	42.87	12.55
	HOMO-2	13.42	12.94	57.91	15.73
	HOMO-1	14.52	41.24	16.10	28.14
	HOMO	10.09	24.87	36.20	28.83
	LUMO	15.40	3.31	65.50	15.79

The vertical electronic transitions for the calculated complexes have been investigated by time-dependent-DFT (TD-DFT) method with the conductor polarizable continuum model (CPCM) to account for solvent effects upon the electronic transition (solvent = CH₃CN). Calculated excitation energies, oscillator strengths, and absorption spectra constructed by convolution of these calculated transitions with Gaussian functions, are depicted in Figure 5. The profiles of the convoluted absorption spectra are similar to those observed experimentally, i.e. moderately intense absorption around 500 nm with absorption shoulder around 600 nm. For clarity, only the calculated vertical transition energies in the visible region are summarized in Table 5. The calculations show two types of one-electron excitation in the visible region: Type 1 - lower energy transitions (ca. 500–600 nm) with oscillator strengths of 10^{-3} , which mainly arise from HOMO–1 → LUMO and HOMO → LUMO transitions; Type 2 - higher energy transitions (ca. 400–500 nm) with oscillator strengths of 10^{-2} – 10^{-1} , which originate from a combination of HOMO–X → LUMO transitions (X = 2–10). It is noted that in each complex the HOMO–1 and HOMO have higher d(Ru) contributions (25–41 %) than that in the LUMO (3 %) whereas the LUMO is dominated by the ON[^]N (61–66 %), therefore Type 1 transition contains d(Ru) → ON[^]N MLCT character. However, the contributions of ON[^]N in the HOMO–1 and HOMO are not low (15–51 %) and this suggests that Type 1 transitions also contain some ON[^]N intra-ligand (IL) character. The HOMO–X are mostly dominated by the ON[^]N (generally > 50 %) with non-neglectable d(Ru) contribution and thus the Type 2 transitions are dominated by ON[^]N intra-ligand (IL) transitions but with some d(Ru) → ON[^]N MLCT component.

Figure 5. Calculated absorption spectra for **2a** and **2b** from TD-DFT/CPCM calculations. Excitation energies and oscillator strengths are shown by the black vertical lines; the spectra (in blue and red) are convoluted with Gaussian function having full width at half maximum (FWHM) of 0.33 eV.

Table 5. Calculated Vertical Transition Energies in the Visible Region for **2a** and **2b** at the TD-DFT/CPCM level

complex	experimental $\lambda_{\max}/\text{cm}^{-1}$ ($\epsilon_{\max}/\text{dm}^3 \text{ mol}^{-1}$ cm^{-1})	TD-DFT calculations	
		excitation energy/ cm^{-1} (oscillator strength)	composition of the excited-state wave functions
2a	16390 (sh, 570)	15730 (0.0043)	$0.63 \Psi_{\text{H} \rightarrow \text{L}} - 0.29 \Psi_{\text{H-1} \rightarrow \text{L}}$
		17280 (0.0024)	$0.49 \Psi_{\text{H-1} \rightarrow \text{L}} - 0.33 \Psi_{\text{H-2} \rightarrow \text{L}} - 0.28 \Psi_{\text{H-3} \rightarrow \text{L}} + 0.22 \Psi_{\text{H} \rightarrow \text{L}}$
	21600 (5860)	20230 (0.0065)	$0.54 \Psi_{\text{H-4} \rightarrow \text{L}} - 0.29 \Psi_{\text{H-3} \rightarrow \text{L}} - 0.22 \Psi_{\text{H-1} \rightarrow \text{L}} - 0.15 \Psi_{\text{H-5} \rightarrow \text{L}} + 0.12 \Psi_{\text{H-9} \rightarrow \text{L}}$
		22400 (0.1438)	$0.61 \Psi_{\text{H-2} \rightarrow \text{L}} + 0.27 \Psi_{\text{H-1} \rightarrow \text{L}} + 0.17 \Psi_{\text{H} \rightarrow \text{L}}$
		24340 (0.0716)	$0.55 \Psi_{\text{H-3} \rightarrow \text{L}} + 0.36 \Psi_{\text{H-4} \rightarrow \text{L}} + 0.18 \Psi_{\text{H-1} \rightarrow \text{L}}$
2b	16340 (sh, 980)	15240 (0.0088)	$0.51 \Psi_{\text{H-1} \rightarrow \text{L}} + 0.46 \Psi_{\text{H} \rightarrow \text{L}} + 0.11 \Psi_{\text{H-2} \rightarrow \text{L}}$
		15890 (0.0088)	$0.41 \Psi_{\text{H-1} \rightarrow \text{L}} - 0.40 \Psi_{\text{H} \rightarrow \text{L}} - 0.27 \Psi_{\text{H-2} \rightarrow \text{L}} - 0.25 \Psi_{\text{H-3} \rightarrow \text{L}} - 0.12 \Psi_{\text{H-4} \rightarrow \text{L}}$
	20660 (5610)	18970 (0.0537)	$0.32 \Psi_{\text{H-3} \rightarrow \text{L}} + 0.30 \Psi_{\text{H-5} \rightarrow \text{L}} + 0.29 \Psi_{\text{H-2} \rightarrow \text{L}} - 0.26 \Psi_{\text{H} \rightarrow \text{L}} + 0.25 \Psi_{\text{H-4} \rightarrow \text{L}} + 0.21 \Psi_{\text{H-1} \rightarrow \text{L}} - 0.11 \Psi_{\text{H-10} \rightarrow \text{L}} - 0.10 \Psi_{\text{H-6} \rightarrow \text{L}}$
		21000 (0.0846)	$0.52 \Psi_{\text{H-2} \rightarrow \text{L}} - 0.32 \Psi_{\text{H-5} \rightarrow \text{L}} - 0.22 \Psi_{\text{H-4} \rightarrow \text{L}} - 0.20 \Psi_{\text{H} \rightarrow \text{L}}$
		23900 (0.0197)	$0.49 \Psi_{\text{H-4} \rightarrow \text{L}} - 0.47 \Psi_{\text{H-3} \rightarrow \text{L}} + 0.13 \Psi_{\text{H-2} \rightarrow \text{L}}$

Although the formal oxidation state for the Ru centers in **2a**, **2b**, and $[\text{Ru}(\text{bpy})([14]\text{aneS4})]^{2+}$ are +2, their partial charges calculated by natural population analysis (NPA)⁴² are much lower due to the ligand-to-metal donation (Table 6). It is noted that the amount of positive charge on the Ru centers and the $[\text{Ru}([14]\text{aneS4})]$ moieties in **2a** and **2b** are larger than that in $[\text{Ru}(\text{bpy})([14]\text{aneS4})]^{2+}$, suggesting that ON[^]N are better electron acceptors than bpy.

Table 6. Natural Population Analysis (NPA)-Derived Partial Charges for **2a**, **2b**, and $[\text{Ru}(\text{bpy})([14]\text{aneS4})]^{2+}$

	2a	2b	$[\text{Ru}(\text{bpy})([14]\text{aneS4})]^{2+}$	
atom	partial charge		atom	partial charge
Ru	−0.02	−0.01	Ru	−0.10
N _{NO}	+0.13	+0.12	N _{bpy}	−0.42, −0.44
N _{Py}	−0.44	−0.44		
S _{ax}	+0.44, +0.46	+0.44, +0.45	S _{ax}	+0.45, +0.46
S _{eq}	+0.39, +0.43	+0.39, +0.41	S _{eq}	+0.40, +0.45
O	−0.35	−0.38		
$[\text{Ru}([14]\text{aneS4})]$	+1.62	+1.61	$[\text{Ru}([14]\text{aneS4})]$	+1.50
ON [^] N	+0.38	+0.39	bpy	+0.50

Conclusion

Two series of Ru complexes containing 2-(2-nitrosoaryl)pyridine (ON[^]N) have been prepared by insertion of nitrosonium ion into the Ru–aryl bond of the corresponding cyclometallated Ru(II) complexes. The Ru–(ON[^]N) bonding interaction has been studied by the structural, electrochemical, spectroscopic and theoretical investigation. The ON[^]N ligands behave as bidentate chelate via the two N atoms, and the short Ru–N_{NO} distances (1.942(5)–1.948(4) Å) in **2a** and **2b** suggest that the Ru → N_{NO} backbonding interaction is substantial. On the basis of the structural studies and the $\nu_{\text{N=O}}$, the

coordinated nitrosoarene in the ON[^]N in this work should be assigned as a neutral species (ArNO)⁰ rather than monoanionic radical (ArNO)^{•1-} or dianion (ArNO)²⁻ species. The nitrosated complexes feature moderately intense absorption bands covering the whole visible region, and TD-DFT calculations reveal that the transitions are mixture of d(Ru) → ON[^]N MLCT and ON[^]N intra-ligand (IL) transitions. Natural population analysis (NPA) shows that the amount of positive charge on the Ru centers and the [Ru([14]aneS4)] moieties in **2a** and **2b** are larger than that in [Ru(bpy)([14]aneS4)]²⁺, suggesting that ON[^]N ligands are better electron acceptor than simple aromatic diimines. Since the absorption spectra of the ON[^]N-ligated complexes cover the entire spectral visible region, we envision that the ON[^]N ligands may open opportunities for developing sensitizers for solar energy conversion. Moreover, the non-innocent behavior of the ON[^]N would be of fundamental interest, and studies are currently underway to isolate the reduced form of the ON[^]N-ligated complexes.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed under an argon atmosphere using standard Schlenk techniques unless otherwise stated. All reagents were used as received, and solvents for reactions were purified by PureSolv MD5 solvent purification system. [Ru(bpy)([14]aneS4)](PF₆)₂ and [Ru(PhPy)(CH₃CN)₄](PF₆) were prepared according to literature procedures.^{36,43} Other cyclometalated analogues [Ru(C[^]N)(CH₃CN)₄](PF₆) were synthesized by the same method as [Ru(PhPy)(CH₃CN)₄](PF₆). ¹H, ¹H–¹H COSY and ¹H–¹H NOESY NMR spectra were recorded on Bruker 400 DRX FT-NMR spectrometers. Peak positions were calibrated with solvent residue peaks as internal standard. The ¹H NMR spectra acquired at 293 K for the nitrosated complexes **2a–2d** only show 1 set of signals, although there are two possible ways that the [14]aneS4 coordinates to the [Ru(ON[^]N)] moiety (Scheme 2a). This is because the two conformations of [14]aneS4 upon coordination to the [Ru(ON[^]N)] moiety are interchangeable at 293 K. Variable temperatures ¹H NMR experiments (193–293 K) have been performed on **2c** to investigate the possibility of observing the fluxional behavior of

[14]aneS4. One more set of signals start to appear at 233 K in the aromatic region, but these two sets of signals are not well resolved even at 193 K and hampered the calculation of the fluxional barrier.

Electrospray mass spectrometry was performed on a PE-SCIEX API 3000 triple quadrupole mass spectrometer. Infrared spectra were recorded as KBr plates on a Perkin-Elmer FTIR-1600 spectrophotometer. UV-visible spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Elemental analyses were done on an Elementar Vario EL Analyzer. Cyclic voltammetry was performed with a CH Instrument Model 600C series electrochemical analyzer/workstation. All solutions were degassed with argon before experiments. An Ag/AgNO₃ (0.1 M in CH₃CN) electrode was used as reference electrode, and the $E_{1/2}$ value of the ferrocenium/ferrocene couple (Cp₂Fe⁺⁰) measured in the same solution was used as an internal reference. Mass magnetic susceptibility (χ_g) of **2a** was measured by a Johnson Matthey magnetic susceptibility balance MSB-1.

Nitroso Complexes 2a–2d, 4a and 4b. Excess [NO][BF₄] (5-fold) were added to the cyclometalated precursors (*ca.* 0.1 g) in dry CH₃CN under argon at room temperature. The color changed from yellow to dark red immediately. The reactions were stirred at room temperature for 1 min. The resulting dark red solutions were concentrated and precipitated by the addition of aq. NH₄PF₆ or NaClO₄. (**Caution!** *Perchlorate salts are potentially explosive and should be handled with care and in small amounts*). The dark red precipitates (orange-red for **3a**) were washed with water followed by absolute ethanol and diethyl ether and dried under vacuum. The solids were then recrystallized by slow diffusion of Et₂O into nitromethane solutions to give dark red crystals.

2a(ClO₄)₂. Yield: 0.111 g, 91 %. Anal. Calcd for Ru₄C₂₁H₂₈N₂S₄Cl₂O₉: C, 33.51; H, 3.75; N, 3.72. Found: C, 33.40; H, 3.94; N, 3.88. ¹H NMR (400 MHz, (CD₃)₂CO): δ 2.14–2.21, 2.65–2.77, 2.91–2.98, 3.23–3.49, 3.58–3.64, 3.87–3.99 (m, 20H, [14]aneS4); 7.49 (d, 1H, J = 7.9 Hz, H_b); 7.74–7.85 (m, 2H, H_b + H_g); 8.08 (t, 1H, J = 7.1 Hz, H_c/H_f); 8.41 (t, 1H, J = 7.2 Hz, H_f/H_c); 8.48 (d, 1H, J = 8.0 Hz, H_d/H_e); 8.56 (d, 1H, J = 8.2 Hz, H_e/H_d); 8.83 (d, 1H, J = 5.3 Hz, H_a). IR (KBr, cm⁻¹): $\nu_{\text{N=O}}$ = 1374, $\nu_{\text{Cl-O}}$ = 1084. ESI-MS: m/z 653 [M²⁺+ClO₄⁻].

2b(PF₆)₂. Yield: 0.081 g, 72 %. Anal. Calcd for Ru₁C₂₃H₂₈N₂S₄O₁P₂F₁₂.CH₃NO₂: C, 31.03; H, 3.36; N, 4.53. Found: C, 30.88; H, 3.52; N, 4.75. ¹H NMR (400 MHz, (CD₃)₂CO): δ 2.22–2.29, 2.60–2.71, 2.97–3.15, 3.28–3.45, 3.54–3.97, (m, 20H, [14]aneS4); 7.95 (d, 1H, *J* = 7.3 Hz, H_h); 8.07–8.12 (m, 2H, H_b + H_g); 8.36 (d, 1H, *J* = 8.8 Hz, H_d); 8.50 (d, 1H, *J* = 8.8 Hz, H_e); 8.82 (d, 1H, *J* = 7.7 Hz, H_f); 9.02 (d, 1H, *J* = 8.0 Hz, H_c); 9.21 (d, 1H, *J* = 5.0 Hz, H_a). IR (KBr, cm⁻¹): ν_{N=O} = 1381, ν_{P-F} = 838. ESI-MS: *m/z* 723 [M²⁺+PF₆⁻].

2c(PF₆)₂. Yield: 0.100 g, 85 %. Anal. Calcd for Ru₁C₂₂H₃₀N₂S₄O₁P₂F₁₂.CH₃NO₂: C, 30.08; H, 3.62; N, 4.58. Found: C, 29.92; H, 3.56; N, 4.58. ¹H NMR (400 MHz, CD₃CN): δ 1.79–1.87, 2.36–2.43, 2.54–2.58, 2.89–3.09, 3.17–3.21, 3.31–3.41, 3.56–3.66 (m, 20H, [14]aneS4); 2.49 (s, 3H, CH₃ of ON[^]N); 7.05 (s, 1H, H_g); 7.63 (t, 1H, *J* = 6.1 Hz, H_b); 7.79 (d, 1H, *J* = 8.1 Hz, H_f); 8.14 (d, 1H, *J* = 8.1 Hz, H_e); 8.21 (t, 1H, *J* = 7.7 Hz, H_c); 8.27 (d, 1H, *J* = 8.8 Hz, H_d); 8.39 (d, 1H, *J* = 4.7 Hz, H_a). IR (KBr, cm⁻¹): ν_{N=O} = 1365, ν_{P-F} = 837. ESI-MS: *m/z* 713 [M²⁺+PF₆⁻].

2d(PF₆)₂. Yield: 0.093 g, 82 %. Anal. Calcd for Ru₁C₂₂H₂₇N₂S₄O₁P₂F₁₅.CH₃NO₂: C, 28.40; H, 3.11; N, 4.32. Found: C, 28.54; H, 3.21; N, 4.19. ¹H NMR (400 MHz, CD₃CN): δ 1.81–1.89, 2.40–2.67, 2.87–3.11, 3.19–3.23, 3.34–3.41, 3.57–3.72 (m, 20H, [14]aneS4); 7.27 (d, 1H, *J* = 7.4 Hz, H_g); 7.75 (t, 1H, *J* = 7.4 Hz, H_f); 8.02 (t, 1H, *J* = 7.3 Hz, H_e); 8.31 (d, 1H, *J* = 7.8 Hz, H_d); 8.48 (d, 1H, *J* = 8.6 Hz, H_c); 8.54 (d, 1H, *J* = 8.6 Hz, H_b); 8.60 (s, 1H, H_a). IR (KBr, cm⁻¹): ν_{N=O} = 1379, ν_{P-F} = 839. ESI-MS: *m/z* 766 [M²⁺+PF₆⁻].

4a(PF₆)₂. Yield: 0.082 g, 65%. Anal. Calcd for Ru₁C₂₂H₂₉N₃S₃O₁P₂F₁₂: C, 31.51; H, 3.48; N, 5.01. Found: C, 31.36; H, 3.67; N, 4.96. ¹H NMR (400 MHz, (CD₃)₂CO): δ 1.56 (s, 9H, *t*-Bu); 2.43–2.52, 2.92–3.02, 3.05–3.11, 3.15–3.38, 3.58–3.74 (m, 12H, [9]aneS3); 7.30 (d, 1H, *J* = 7.1 Hz, H_h), 7.80–7.83 (m, 2H, H_b + H_g), 8.11 (t, 1H, *J* = 7.2 Hz, H_c/H_f), 8.39 (t, 1H, *J* = 7.2 Hz, H_f/H_c), 8.48 (d, 1H, *J* = 7.9 Hz, H_d/H_e), 8.55 (d, 1H, *J* = 8.1 Hz, H_e/H_d), 9.02 (d, 1H, *J* = 5.0 Hz, H_a). IR (KBr, cm⁻¹): ν_{C≡N} = 2188, ν_{N=O} = 1396, ν_{P-F} = 834. ESI-MS: *m/z* 693 [M²⁺+PF₆⁻].

4b(ClO₄)₂. Yield: 0.086 g, 63%. Anal. Calcd for Ru₁C₂₄H₂₉N₃S₃Cl₂O₉: C, 37.35; H, 3.79; N, 5.45. Found: C, 37.62; H, 3.84; N, 5.50. (400 MHz, CD₃CN): δ 1.52 (s, 9H, *t*-Bu); 2.18–2.24, 2.36–2.45, 2.53–2.61, 2.74–2.80, 2.85–2.90, 3.06–3.16, 3.22–3.27, 3.42–3.47 (m, 12H, [9]aneS3); 7.59 (d, 1H, *J* = 7.8 Hz, H_h); 7.89–7.92 (m, 1H, H_b); 7.98 (t, 1H, *J* = 7.9 Hz, H_g); 8.18 (d, 1H, *J* = 8.8 Hz, H_d); 8.32 (d, 1H, *J* = 8.9 Hz, H_e); 8.66 (d, 1H, *J* = 7.9 Hz, H_f); 8.79 (dd, 1H, *J* = 8.1, 1.1 Hz, H_c); 9.12 (dd, 1H, *J* = 5.4, 1.3 Hz, H_a). IR (KBr, cm⁻¹): $\nu_{\text{C}\equiv\text{N}}$ = 2185, $\nu_{\text{N}=\text{O}}$ = 1370, $\nu_{\text{Cl}-\text{O}}$ = 1080. ESI-MS: *m/z* 672 [M²⁺+ClO₄⁻].

Scheme 3. Labeling scheme for hydrogen atoms on ON[^]N in complexes **2a–2d** and **4a, 4b**

X-ray Crystallography. X-ray diffraction data for **1a(ClO₄)**, **2a(ClO₄)₂**, and **2b(PF₆)₂•CH₃NO₂** were collected on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer with Cu K α radiation (λ = 1.54178 Å) or Mo K α radiation (λ = 0.71073 Å) at 133 K. The data were processed using CrysAlis.⁴⁴ The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97⁴⁵ within WinGX.⁴⁶ All non-hydrogen atoms were refined anisotropically in the final stage of least-squares refinement. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms. Disorder of the cations in **2a(ClO₄)₂** and **2b(PF₆)₂•CH₃NO₂** were observed, which arise from there being two ways in which the [14]andS4 can coordinate to a [Ru(ON[^]N)] moiety. Disorder of the anions in **2a(ClO₄)₂** and **2b(PF₆)₂•CH₃NO₂** were also observed. Split models, several DFIX and ISOR restraints were applied in the refinement of these crystal structures.

Computational Methodology. DFT calculations were performed on $[\text{Ru}([14]\text{aneS4})(\text{bpy})]^{2+}$, **2a**, and **2b**. Their electronic ground states were optimized without symmetry imposed using Becke's three-parameter hybrid functional with the Lee-Yang-Parr correlation functional (B3LYP).^{38,39} The ECP28MDF pseudopotential was employed for the Ru atoms with the correlation consistent cc-pVTZ-PP basis set of Peterson *et al.*⁴⁰ The 6-31+G* basis set was employed for C, H, N, O, and S atoms.⁴¹ Tight SCF convergence (10^{-8}au) was used for all calculations. Frequency calculations were also performed on all the optimized structure. As no imaginary vibrational frequencies were encountered, the optimized stationary points were confirmed to be local minima. The vertical transition energies for **2a** and **2b** in CH_3CN were computed at their respective gas-phase optimized ground-state geometries using time-dependent-DFT (TD-DFT) method with the same density functional and basis sets in the geometry optimizations. The conductor polarizable continuum model (CPCM)⁴⁷ was used to account for solvent effects upon the electronic transition. Natural population analysis was performed using NBO 3.0⁴² implemented to Gaussian 09. All the calculations were performed using the Gaussian 03 program package (revision D.01).⁴⁸

ACKNOWLEDGMENT. The work described in this paper was supported by grants from City University of Hong Kong (Project Nos. 7008034 and 7002591). We are grateful to Dr. Shek-Man Yiu for X-ray diffraction data collection.

Supporting_Information. Synthetic procedures for cyclometalated complexes **1a–1d**, **3b**; optimized geometries for **2a**, **2b**, and $[\text{Ru}([14]\text{aneS4})(\text{bpy})]^{2+}$; plots of molecular orbital surfaces which are of spectroscopic importance for **2a** and **2b**; crystallographic information files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES

- (1) Kirby, G. W. *Chem. Soc. Rev.* **1977**, 6, 1.
- (2) Zuman, P.; Shah, B. *Chem. Rev.* **1994**, 94, 1621.
- (3) Momiyama, N.; Yamamoto, H. *Org. Lett.* **2002**, 4, 3579.
- (4) Adam, W.; Krebs, O. *Chem. Rev.* **2003**, 103, 4131.
- (5) Gowenlock, B. G.; Richter-Addo, G. B. *Chem. Rev.* **2004**, 104, 3315.
- (6) Gowenlock, B. G.; Richter-Addo, G. B. *Chem. Soc. Rev.* **2005**, 34, 797.
- (7) Yamamoto, H.; Momiyama, N. *Chem. Commun.* **2005**, 3514.
- (8) Yamamoto, Y.; Yamamoto, H. *Eur. J. Org. Chem.* **2006**, 2031.
- (9) Payette, J. N.; Yamamoto, H. *J. Am. Chem. Soc.* **2008**, 130, 12276.
- (10) Loeb, R. F.; Bock, A. V.; Fitz, R. *Am. J. Med. Sci.* **1921**, 161, 539.
- (11) Chottard, G.; Mansuy, D. *Biochem. Biophys. Res. Commun.* **1977**, 77, 1333.
- (12) Alston, T. A.; Porter, D. J. T.; Bright, H. J. *Acc. Chem. Res.* **1983**, 16, 418.
- (13) Kazanis, S.; McClelland, R. A. *J. Am. Chem. Soc.* **1992**, 114, 3052.
- (14) Stone, J. R.; Marletta, M. A. *Biochemistry* **1995**, 34, 16397.
- (15) Little, R. G.; Doedens, R. J. *Inorg. Chem.* **1973**, 12, 537.
- (16) Cameron, M.; Gowenlock, B. G. *Chem. Soc. Rev.* **1990**, 19, 355.
- (17) Wang, L.-S.; Chen, L.; Khan, M. A.; Richter-Addo, G. B. *Chem. Commun.* **1996**, 323.
- (18) Fox, S. J.; Chen, L.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1997**, 36, 6465.

- (19) Richter-Addo, G. B. *Acc. Chem. Res.* **1999**, *32*, 529.
- (20) Godbout, N.; Sanders, L. K.; Salzmann, R.; Havlin, R. H.; Wojdelski, M.; Oldfield, E. *J. Am. Chem. Soc.* **1999**, *121*, 3829.
- (21) Lee, J.; Chen, L.; West, A. H.; Richter-Addo, G. B. *Chem. Rev.* **2002**, *102*, 1019.
- (22) Lee, J.; Twamley, B.; Richter-Addo, G. B. *Dalton Trans.* **2004**, 189.
- (23) Labios, L. A.; Millard, M. D.; Rheingold, A. L.; Figueroa, J. S. *J. Am. Chem. Soc.* **2009**, *131*, 11318.
- (24) Mansuy, D.; Battioni, P.; Chottard, J.-C.; Riche, C.; Chiaroni, A. *J. Am. Chem. Soc.* **1983**, *105*, 455.
- (25) Rehorek, D. *Chem. Soc. Rev.* **1991**, *20*, 341.
- (26) Iwasa, T.; Shimada, H.; Takami, A.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *Inorg. Chem.* **1999**, *38*, 2851.
- (27) Askari, M. S.; Girard, B.; Murugesu, M.; Ottenwaelder, X. *Chem. Commun.* **2011**, *47*, 8055.
- (28) Tomson, N. C.; Labios, L. A.; Weyhermüller, T.; Figueroa, J. S.; Wieghardt, K. *Inorg. Chem.* **2011**, *50*, 5763.
- (29) Chan, S.-C.; Pat, P.-K.; Lau, T.-C.; Wong, C.-Y. *Organometallics* **2011**, *30*, 1311.
- (30) Efraty, A.; Elbaze, G. *J. Organomet. Chem.* **1984**, *260*, 331.
- (31) Conroy-Lewis, F. M.; Redhouse, A. D.; Simpson, S. J. *J. Organomet. Chem.* **1990**, *399*, 307.
- (32) Shaver, A.; El-khateeb, M.; Lebuis, A.-M. *Inorg. Chem.* **1995**, *34*, 3841.
- (33) Diversi, P.; Fontani, M.; Fuligni, M.; Laschi, F.; Matteoni, S.; Pinzino, C.; Zanello, P. *J. Organomet. Chem.* **2001**, *626*, 145.

- (34) Hadadzadeh, H.; DeRosa, M. C.; Yap, G. P. A.; Rezvani, A. R.; Crutchley, R. J. *Inorg. Chem.* **2002**, *41*, 6521.
- (35) Wong, C.-Y.; Lai, L.-M.; Leung, H.-F.; Wong, S.-H. *Organometallics* **2009**, *28*, 3537.
- (36) Adams, H.; Amado, A. M.; Félix, V.; Mann, B. E.; Antelo-Martinez, J.; Newell, M.; Ribeiro-Claro, P. J. A.; Spey, S. E.; Thomas, J. A. *Chem. Eur. J.* **2005**, *11*, 2031.
- (37) Liang J.-L.; Huang, J.-S.; Zhou, Z.-Y.; Cheung, K.-K.; Che, C.-M. *Chem. Eur. J.* **2001**, *7*, 2306.
- (38) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (39) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785.
- (40) Peterson, K.; Figgen, D.; Dolg, M.; Stoll, H. *J. Chem. Phys.* **2007**, *126*, 124101.
- (41) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Francel, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
- (42) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
- (43) Fernandez, S.; Pfeiffer, M.; Ritleng, V.; Sirlin, C. *Organometallics* **1999**, *18*, 2390.
- (44) CrysAlis, Oxford Diffraction Ltd., Version 1.171.31.8, 2007.
- (45) Sheldrick, G. M. SHELXS-97 and SHELXL-97, *Program for Crystal Structure Solution and Refinements*; University of Göttingen: Germany, 1997.
- (46) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
- (47) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.
- (48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi,

J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, revision D.01*; Gaussian, Inc.: Wallingford, CT, 2004.

Table of Contents

Ruthenium complexes containing 2-(2-nitrosoaryl)pyridine ($\text{ON}^{\wedge}\text{N}$) have been prepared by insertion of NO^+ into the Ru–aryl bond of cyclometallated Ru(II) complexes. Structural, spectroscopic, electrochemical and theoretical investigations suggest that the coordinated $\text{ON}^{\wedge}\text{N}$ ligands are neutral moieties $(\text{ArNO})^0$ and are better electron acceptors than 2,2'-bipyridine. The electronic absorptions associated with the complexes in the visible region are assigned as a mixing of $d(\text{Ru}) \rightarrow \text{ON}^{\wedge}\text{N}$ metal-to-ligand charge transfer and $\text{ON}^{\wedge}\text{N}$ intra-ligand transitions.