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Syntheses, structures and properties of ruthenium complexes of tridentate ligands: isolation and characterization of a rare example of ruthenium nitrosyl complex containing {RuNO}^{5} moiety†‡

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Novel ruthenium complexes [Ru(L^1)(NO)Cl_2] (**1**), [Ru(L^2)(PPh_3)Cl_2] (**2**), [Ru(L^2)(PPh_3)(NO_2)Cl] (**3**) and [Ru(L^2)(PPh_3)(NO)Cl](ClO_4)$_2$ (**4**) (where L^1H = *N*′-phenyl-*N*′-(pyridin-2-yl)picolinohydrazide and L^2 = (1-phenyl-1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)hydrazine) were synthesized. These complexes were characterized by using IR, UV-Vis, elemental analysis, electrochemical and NMR spectral studies. The molecular structures of nitrosyl complexes **1** and **4** were determined by X-ray crystallographic studies. Complexes **1** and **4** readily released NO under visible and ultraviolet light and free NO was transferred to reduced myoglobin. The amount of photoreleased NO was estimated using Griess reagent assay. During photolysis of NO, the generation of reactive nitrogen or/and reactive oxygen species was determined by DPPH (2,2-diphenyl-1-picrylhydrazine) radical quenching studies under aerobic conditions. A paramagnetic complex [Ru(L^2)(PPh_3)(NO)Cl](NO_3)$_3$ (**5**) was synthesized *via* chemical oxidation of **4** with an excess of ceric ammonium nitrate (CAN) in acetonitrile. Complex **5** was characterized by UV-Vis, IR, elemental analysis and EPR spectral studies which authenticated the presence of the {RuNO}^{5} moiety in **5**. Theoretical investigation by DFT calculation supported the oxidation of complex **4** having {RuNO}^{6} species and the formation of **5** containing {RuNO}^{5}.

Introduction

The coordination chemistry of non-innocent ligand nitric oxide (NO) and the synthesis of designed metal nitrosyl complexes have received considerable attention in the recent past.[1–8] A special feature of metal nitrosyl complexes is the targeted specific delivery of nitric oxide on demand as NO is involved in various physiological processes and it executes biological activities which are concentration dependent.[2c] This also implies that delivery[2,4] as well as scavenging[6] of NO are important for the concentration dependent biochemistry of nitric oxide. Among inorganic complexes, sodium nitroprusside (SNP) and Raussin's salts are well known NO donors[2b,d] used for the regulation of blood pressure. However, ruthenium nitrosyl complexes are better options for controlled delivery of NO.[2–5] On the other hand, ruthenium complexes have also been used for the scavenging of NO.[6] For these reasons, there is upsurge of interest in the synthesis and biological activity studies of ruthenium nitrosyl complexes.

Due to the non-innocent behaviour of ligand NO, Enemark and Feltham[8] formulated {RuNO}^{x} notation for ruthenium nitrosyl complexes where *x* stands for number of d-electrons present in the metal *plus* a single electron for NO˙. Investigation of the literature revealed that there are reports on ruthenium nitrosyl complexes having {RuNO}^{6},[2–7] {RuNO}^{7},[2b,4a] and {RuNO}^{8} moieties.[4a,9] However to the best of our knowledge, there is only a single report by Kaim and coworkers available in the literature for ruthenium complex containing {RuNO}^{5} species.[10] This was also discussed recently by Kaim and Lahiri.[4a] Kaim and his coworkers generated a complex [Cl_5Ru(NO)]$^-$, having a {RuNO}^{5} moiety, in solution electrochemically and characterized it by IR and EPR spectral studies. These data prompted us to isolate and characterize ruthenium nitrosyl complexes having a {RuNO}^{5} moiety *via* the rational designing of ligands, followed by synthesis of ruthenium nitrosyl complexes derived from those ligands.

Considering the difficulties of direct synthesis of ruthenium nitrosyls having {RuNO}^{5} species, we adopted the following

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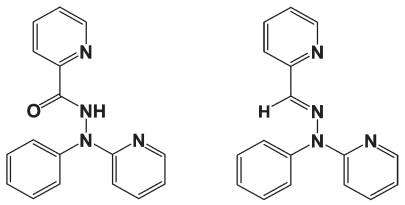
†Dedicated to Prof. Pradip K. Mascharak on his 60th birthday.

‡Electronic supplementary information (ESI) available: Characterization of complexes by electronic, infrared and NMR spectral studies. X-ray crystallographic data of complexes **1** and **4** in CIF format. CCDC 880432 for **1**, 880433 for **4**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt00027c



L^1H L^2

Scheme 1 Schematic drawing of ligands.

strategy. It is well known in the literature that carboxamido nitrogen stabilizes a higher oxidation state of the metal center[11] and we designed and synthesized ligand L^1H (*N*′-phenyl-*N*′-(pyridin-2-yl)picolinohydrazide, Scheme 1). We expected that the synthesis of a ruthenium nitrosyl complex having $\{RuNO\}^6$ species would be easy and the most probable description of $\{RuNO\}^6$ would be $\{Ru^{II}NO^+\}^6$. Next, we could easily accomplish oxidation of the complex which will lead to the formation of a nitrosyl complex containing the $\{RuNO\}^5$ moiety. Carboxamido nitrogen will favour the stability of Ru(III) and NO will bind to the metal as NO^+ and hence the combination of Ru(III) and NO^+ may give rise to the generation of a nitrosyl complex having a $\{RuNO\}^5$ species. To understand the role of carboxamido nitrogen, we decided to synthesize in parallel another ligand, L^2 (1-phenyl-1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)hydrazine), where an imine nitrogen was present instead of an amide nitrogen (Scheme 1).[11]

Herein we report the synthesis and characterization of ruthenium complexes $[Ru(L^1)(NO)Cl_2]$ (**1**), $[Ru(L^2)(PPh_3)Cl_2]$ (**2**), $[Ru(L^2)(PPh_3)(NO_2)Cl]$ (**3**) and $[Ru(L^2)(PPh_3)(NO)Cl](ClO_4)_2$ (**4**) derived from the described ligands (L^1H and L^2). The photochemical properties of the nitrosyl complexes were examined and the amount of photolytically cleaved NO was estimated by using a Griess reagent reaction. DPPH (2,2-diphenyl-1-picrylhydrazine) radical quenching assay was performed to detect the amount of generated reactive nitrogen and/or reactive oxygen species during photolysis of NO under aerobic conditions. Redox properties of the complexes were investigated and we isolated a novel complex $[Ru(L^2)(PPh_3)(NO)Cl](NO_3)_3$ (**5**) having $\{RuNO\}^5$ moiety and characterized by UV-Vis, IR and EPR spectral studies.

Experimental section

Materials

All the reagents were of analytical grade and were used as obtained. $RuCl_3{\cdot}3H_2O$ was purchased from Loba Chemie Pvt. Ltd, Mumbai, India. Double distilled water and distilled solvents were used in all the experiments. Equine skeletal muscle myoglobin was obtained from Sigma Aldrich, Steinheim, Germany.

Physical measurements

Infrared spectra were obtained on KBr pellets with a Thermo Nicolet Nexus FTIR spectrometer, using 16 scans and were reported in cm^{-1}. Electronic absorption spectra of all the complexes were recorded in dichloromethane and acetonitrile solvents with an Evolution 600, Thermo Scientific UV-Vis spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on a Bruker AVANCE, 500.13 MHz spectrometer in the deuterated solvents. Cyclic voltammetric studies were performed on a CH-600 electroanalyser in dichloromethane with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The working electrode, reference electrode and auxiliary electrode were a glassy carbon electrode, an Ag/AgCl electrode and a Pt wire respectively. The concentration of the compounds was in the order of 10^{-3} M. The ferrocene/ferrocenium couple occurred at $E_{1/2}$ = + 0.54 (70) V *vs*. Ag/AgCl (scan rate 0.1 V s^{-1}) in dichloromethane under the same experimental conditions. EPR measurement was done using a 9.5 GHz JEOL spectrometer operated at X-band frequency.

X-ray crystallography

Orange-red crystals of **1** and **4** were obtained by slow evaporation of solution from the complexes in a CH_2Cl_2–methanol mixture. The X-ray data collection and processing for complexes were performed on a Bruker Kappa Apex-II CCD diffractometer by using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 273 K for **1** and at 293 K for **4**. Crystal structures were solved by direct methods. Structure solutions, refinement and data output were carried out with the SHELXTL program.[12,13] 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.[14]

Synthesis of metal complexes

L^1H and L^2 were synthesized according to the procedure reported earlier.[11] The precursor complex $[Ru(PPh_3)_3Cl_2]$ was also prepared by following the reported procedure.[5]

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.

Synthesis of $[Ru(L^1)(NO)Cl_2]$ (1). First, a batch of $NaNO_2$ (0.070 g, 1 mmol) was added to a hot methanolic solution (20 mL) of $Ru(PPh_3)_3Cl_2$ (0.096 g, 0.1 mmol). The mixture was heated under reflux for 30 minutes. The brown colour of solution was turned to reddish yellow. Now 0.5 mL of perchloric acid ($HClO_4$) was added to the same solution. Then ligand L^1H (0.043 g, 0.15 mmol) was mixed to the same solution to obtain complex **1** (yield: 45%). Anal. Calcd for $C_{17}H_{13}Cl_2N_5O_2Ru$ (491.29): C, 41.56; H, 2.67; N, 14.25. Found: C, 43.38; H, 2.93; N, 13.97. IR (KBr disk, cm^{-1}): 1871 (ν_{NO}), 1654 (ν_{CONH}) cm^{-1}. UV-Vis (CH_2Cl_2; λ_{max}/nm (ε, M^{-1} cm^{-1})): 302 (9670), 383 (3291), 442 (2400). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.25 (d, 1H), 7.95 (q, 2H), 7.85 (m, 1H), 7.73 (d, 2H), 7.57–7.42 (m, 5H), 6.82 (t, 1H) and 6.63 (d, 1H) ppm.

$[Ru(L^2)(PPh_3)Cl_2]$ (2). A batch of (0.045 g, 0.15 mmol) of L^2 was added directly to a solution of $Ru(PPh_3)_3Cl_2$ (0.095 g, 0.1 mmol) in 20 mL of degassed benzene. The colour of solution was changed to pink from brown red colour. This solution

was refluxed for 1.5 h under a nitrogen atmosphere. A solid of pink colour was precipitated out, which was then filtered out and washed thoroughly with hexane and benzene (yield: 91.8%). Anal. Calcd for $C_{35}H_{29}Cl_2N_4PRu$ (708.58): C, 59.33; H, 4.13; N, 7.91. Found: C, 62.12; H, 5.11; N, 6.97. IR (KBr disk, in cm^{-1}): 1625, 1598 ($\nu_{C=N}$), 1481, 1456, 1434, 765, 696, 523 (ν_{PPh3}) cm^{-1}. UV-Vis (CH_2Cl_2; λ_{max}/nm (ε, M^{-1} cm^{-1})): 506 (3191), 336 (16 950), 234 (27 163). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.73 (d, 1H), 8.62 (d, 1H), 7.44–6.92 (m, 23H), 6.88 (d, 1H), 6.72 (t, 1H), 6.57 (s, 1H) and 5.83 (d, 1H) ppm. ^{31}P NMR ($CDCl_3$, 500 MHz): δ 41.97 ppm.

Synthesis of $[Ru(L^2)(PPh_3)(NO_2)Cl]$ (3). To a solution of complex **2** (0.071 g, 0.1 mmol) with 20 mL of methanol, a batch of $NaNO_2$ (0.070 g, 1 mmol) was added. The mixture was heated under reflux for 20–30 minutes to obtain a solution of yellowish red colour. The mixture was filtered and was kept for 2–3 days to get a precipitate of complex **3** (yield: 68.66%). Anal. Calcd for $C_{35}H_{29}ClN_5O_2PRu$ (719.13): C, 58.46; H, 4.06; N, 9.74. Found: C, 58.11; H, 3.54; N, 11.47. IR (KBr disk, cm^{-1}): 1603, 1570, 1360, 1300 (ν_{NO2}), 746, 694, 522 (ν_{PPh3}) cm^{-1}. UV-Vis (CH_2Cl_2; λ_{max}/nm (ε, M^{-1} cm^{-1})): 323 (22 428), 451 (4036). ^1H NMR ($CDCl_3$, 500 MHz): δ 9.52 (d, 1H), 9.37 (d, 1H), 7.6 (m, 4H), 7.4 (t, 1H), 7.34–7.12 (m, 17H), 6.88 (d, 4H) and 5.95 (d, 1H) ppm. ^{31}P NMR ($CDCl_3$, 500 MHz): δ 39.19 ppm.

Synthesis of $[Ru(L^2)(PPh_3)(NO)Cl](ClO_4)_2$ (4). A batch of complex **3** (0.14 g, 0.2 mmol) with 20 mL of methanol was acidified with 0.5 mL of perchloric acid ($HClO_4$). The yellowish red colour of the solution was turned to light yellow colour. The solution mixture was kept in the dark for 3 days to obtain a crystalline solid of complex **4** (yield: 73.64%). Anal. Calcd for $C_{35}H_{29}Cl_3N_5O_9PRu$ (902.04): C, 46.60; H, 3.24; N, 7.76. Found: C, 46.77; H, 2.32; N, 7.81. IR (KBr disk, cm^{-1}): 1890 (ν_{NO}), 1092, 623 (ν_{ClO4}), 746, 694, 522 (ν_{PPh3}) cm^{-1}. UV-Vis (CH_3CN; λ_{max}/nm (ε, M^{-1} cm^{-1})): 274 (25 550), 425 (4270). ^1H NMR (CD_3CN, 500 MHz): δ 8.79 (d, 1H), 8.31 (d, 1H), 8.09 (t, 1H), 7.89–7.35 (m, 25H), and 6.43 (d, 1H) ppm. ^{31}P NMR (CD_3CN, 500 MHz): δ 26.75 ppm.

Synthesis of $[Ru(L^2)(PPh_3)(NO)Cl](NO_3)_3$ (5). Complex **4** (0.09 g, 0.1 mmol) was dissolved in 25 mL of acetonitrile. Now a 5 mL acetonitrile solution of ceric ammonium nitrate (0.44 g, 0.8 mmol) was added dropwise to the same solution. The initial yellowish red colour of the solution was gradually changed to dark red. The precipitation of complex **5** was obtained when 20 mL diethyl ether was added to the acetonitrile solution. The mixture was filtered and washed with diethyl ether and was dried (yield: 62.24%). Anal. Calcd for $C_{35}H_{29}ClN_8O_{10}PRu$ (889.15): C, 47.28; H, 3.29; N, 12.60. Found: C, 46.88; H, 2.31; N, 11.38. IR (KBr disk, cm^{-1}): 1910 (ν_{NO}), 1391 (ν_{NO3}), 1085, 750, 695, 518 (ν_{PPh3}) cm^{-1}. UV-Vis (CH_3CN; λ_{max}/nm (ε, M^{-1} cm^{-1})): 272 (10 835).

Myoglobin trapping experiment

50 mM phosphate buffer solution of pH 6.8 was prepared by adding 0.4192 g of $NaH_2PO_4{\cdot}2H_2O$ and 0.3283 g of anhydrous Na_2HPO_4 to 50 mL of MilliQ water and making the volume up to 100 mL in a volumetric flask. 5 mg equine skeletal muscle myoglobin was dissolved in 5 mL of the above prepared buffer solution.

Griess reagent assay

The photodissociation of nitric oxide from **1** and **4** was also confirmed by estimating its amount using the Griess reagent (GR).[5a,15] The reagent was freshly prepared by mixing equal volumes of 1% sulphanilamide in 5% orthophosphoric acid and 0.1% naphthylethylenediamine dihydrochloride (NED) in distilled water. The estimation of NO or nitrite (NO_2^-) ion was measured by observing the increase in the absorbance at ~538 nm due to the formation of azo dye.

DPPH quenching studies

Disappearance of colour was observed during the estimation of antioxidant properties by DPPH (2,2-diphenyl-1-picrylhydrazine) radical.[16–19] Electronic spectra were recorded in acetonitrile solutions. The UV-Vis spectrum of DPPH radical (~10^{-5} M) showed a band near 520 nm. There was no reaction when 100 μM solutions of **1** and **4** were treated with the solution of DPPH radical in dark conditions. However, exposure of UV light to the same solutions resulted in the disappearance of the peak near 520 nm which indicated the release of NO radical from the nitrosyls.

Quantum yield measurements

Standard ferrioxalate actinometer (0.006 M solution of potassium ferrioxalate in 0.1 N H_2SO_4) was used to determine the intensity of the UV light (λ_{irr} = 365 nm). Quantum yields (Φ_{NO}) of photorelease of NO for complexes **1** and **4** were determined from the decrease in their absorption bands with λ_{max} near 456 nm and 426 nm respectively when irradiated with the light of a UV lamp (λ_{irr} = 365 nm) and were calculated by following the procedure reported earlier.[5a]

DFT study and computational details

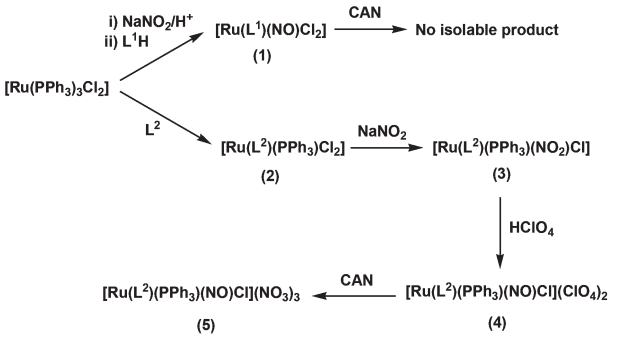
The DFT calculation for complex **4** was carried out using Gaussian 03 program package.[20,21] The Becke's three parameters hybrid exchange functional with the Lee–Yang–Parr (LYP) nonlocal correlation functional was used throughout the computational study.[20,21] A LANL2DZ basis set[21] for ruthenium metal was used in the calculation. The NO stretching frequency was calculated using a scaling factor of 0.97 for LANL2DZ basis set.[22] The X-ray coordinates of the complex were used as input data for the geometry optimisation. The Gauss View-4 program was used for pictorial representation of spin densities and frontier molecular orbitals. Time dependent density functional theory (TD-DFT) calculations were also employed on the optimised geometries to evaluate the electronic transitions.

Results and discussion

Synthesis

We have utilized $[Ru(PPh_3)_3Cl_2]$ as a starting material[5] during the synthesis of our ruthenium complexes. Treatment of

acidified nitrite solution with $[Ru(PPh_3)_3Cl_2]$ gave rise to a solution of orange-yellow colour. The addition of a methanolic solution of L^1H to this solution afforded nitrosyl complex $[Ru(L^1)(NO)Cl_2]$ (**1**). Similarity of the ligand L^2 with 2,2′,2″-terpyridine (trpy) prompted us to synthesize complex $[Ru(L^2)(PPh_3)(NO)Cl](ClO_4)_2$ (**4**) by following the procedure reported earlier.[23] Reaction of $[Ru(PPh_3)_3Cl_2]$ with L^2 afforded complex $[Ru(L^2)(PPh_3)Cl_2]$ (**2**) in benzene under nitrogen atmosphere. Complex **2** was refluxed with $NaNO_2$ in methanol and we isolated and characterized complex $[Ru(L^2)(PPh_3)(NO_2)Cl]$ (**3**). This complex upon acidification ($HClO_4$, in excess) gave rise to nitrosyl complex $[Ru(L^2)(PPh_3)(NO)Cl](ClO_4)_2$ (**4**). Complexes were isolated in good yield and the synthetic procedures described above have been summarized in Scheme 2. Complex $[Ru(L^2)(PPh_3)(NO)Cl](NO_3)_3$ (**5**) was synthesized *via* chemical oxidation of **4** by excess of ceric ammonium nitrate (CAN) and will be discussed later. All the complexes were found to be soluble in most of the organic solvents such as dichloromethane, acetonitrile, methanol, benzene and dimethylformamide.



Scheme 2 Synthetic routes for complexes **1–5** (CAN = ceric ammonium nitrate).

Description of structures

The molecular structures of complexes $[Ru(L^1)(NO)Cl_2]$ (**1**) and $[Ru(L^2)(PPh_3)(NO)Cl](ClO_4)_2$ (**4**) were determined by using X-ray crystallographic studies (Table 1) and are displayed in Fig. 1 and 2 respectively. In both the complexes, the geometry around the metal center was found to be distorted octahedral. In the molecular structure of **1**, carboxamido nitrogen (N2), two pyridine nitrogens (N1 and N4) along with N5(NO) constituted the equatorial plane whereas two chlorine atoms (Cl1 and Cl2) were found at the axial positions *trans* to each other.

In the molecular structure of **4**, imine nitrogen (N3), two pyridine nitrogens (N2 and N4) and N1(NO) were observed at the equatorial positions however one phosphine group and one chlorine (Cl1) atom occupied the axial positions *trans* to each other.

Meridional spanning of ligands was found in the complexes. Interestingly, NO was found to be *trans* to the amide nitrogen (N2) for **1** whereas it occupied a *trans* position with respect to the imine nitrogen (N3) for **4** and these gave rise to a similar equatorial N_4 coordination for the metal center.

Ru–N(NO) distances (1.761(2) Å in **1** and 1.731(4) Å in **4**) were found to be consistent with the values reported in the literature (Table 2).[2,4] The N–O distances (1.147(3) Å in **1** and 1.142(4) Å in **4**) were also found to be consistent with the

Table 1 Crystal data and structural refinement parameters for complexes $[Ru(L^1)(NO)Cl_2]$ (**1**) and $[Ru(L^2)(PPh_3)(NO)Cl](ClO_4)_2$ (**4**)

	1	**4**
Empirical formula	$C_{17}H_{13}Cl_2N_5O_2Ru$	$C_{35}H_{29}Cl_3N_5O_9PRu$
Formula weight	491.29	902.02
Temperature/K	273(2)	293(2)
Λ (Å) (Mo-Kα)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P21/c$	$P\bar{1}$
a (Å)	8.6701(3)	10.332(2)
b (Å)	27.3657(10)	13.149(3)
c (Å)	8.7172(3)	15.401(3)
α (°)	90.00	89.076(12)
γ (°)	90.00	67.489(10)
β (°)	115.417(2)	76.191(11)
V (Å^3)	1868.08(12)	1870.4(7)
Z	4	2
ρ_{calc} (g cm^{-3})	1.747	1.602
F (000)	976.0	912.0
θ range	2.34–27.45	2.24–27.56
Index ranges	$-11 < h < 11$, $-35 < k < 35$, $-11 < l < 11$	$-13 < h < 13$, $-17 < k < 17$, $-20 < l < 17$
Data/restraints/par.	4361/0/244	8758/7/500
GOF[a] on F^2	0.976	1.374
R_1[b] [$I > 2\sigma(I)$]	0.0357	0.0583
R_1 [all data]	0.0556	0.1192
wR_2[c] [$I > 2\sigma(I)$]	0.0724	0.0825
wR_2 [all data]	0.0792	0.0908

[a] GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/M - N]^{1/2}$ (M = number of reflections, N = number of parameters refined). [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(F_o^2)^2]]^{1/2}$.

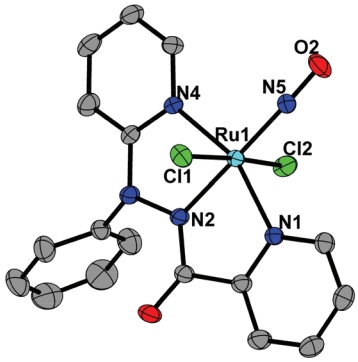


Fig. 1 ORTEP diagram (30% probability level) of complex $[Ru(L^1)(NO)Cl_2]$ (**1**). Hydrogen atoms are not shown for clarity.

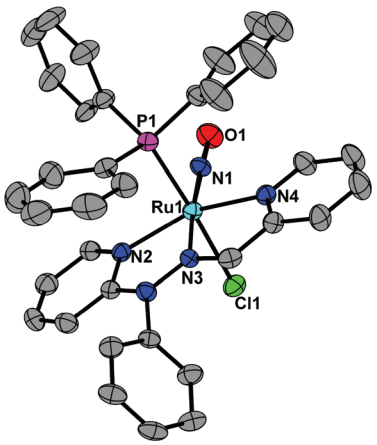


Fig. 2 ORTEP diagram (30% probability level) of the cation of complex $[Ru(L^2)(PPh_3)(NO)Cl](ClO_4)_2$ (**4**). Hydrogen atoms are not shown for clarity.

reported values.[2,4] The N–O stretching frequencies and N–O distances along with Ru–N–O angles (~170° in **1** and ~174° in **4**) clearly expressed $\{Ru^{II}–NO^{+}\}^6$ description[2b] of $\{Ru–NO\}^6$ moieties in **1** and **4**. The presence of a phosphine group was also supported by ^{31}P NMR data in complex **4** (*vide infra*).

The structures of complexes $[Ru(L^2)(PPh_3)Cl_2]$ (**2**) and $[Ru(L^2)(PPh_3)(NO_2)Cl]$ (**3**) were established by NMR spectral studies (Fig. S1–S4 and Table S1‡). The expected multiple signals were observed in the range 6.5–7.8 ppm in ^1H NMR spectra of both the complexes. The single peaks at ~42.0 ppm and ~39.0 ppm in ^{31}P NMR spectra of **2** and **3** respectively clearly indicated the presence of one PPh_3 group.[23]

Spectral studies

The nitrosyl complexes **1** and **4** were found to be diamagnetic having a bivalent state of ruthenium metal in them which was confirmed by ^1H and ^{31}P NMR spectral studies (shown in ESI‡). ^1H NMR spectra of complexes **1** and **4** (Fig. S5, S6 and Table S1‡) indicated their $S = 0$ ground state in nitrosyl complexes.[5,8] In ^{31}P NMR spectrum of **4**, the peak near 27.0 ppm confirmed the presence of a PPh_3 group (shown in Fig. S7‡).

Table 2 Selected bond distances and bond angles of complexes $[Ru(L^1)(NO)Cl_2]$ (**1**) and $[Ru(L^2)(PPh_3)(NO)Cl](ClO_4)_2$ (**4**)

Bond lengths (Å)		Bond angles (°)	
1			
Ru(1)–Cl(1)	2.3678(8)	N(1)–Ru(1)–N(4)	157.61(8)
Ru(1)–Cl(2)	2.3882(8)	N(2)–Ru(1)–N(5)	173.51(10)
Ru(1)–N(2)	1.977(2)	Cl(1)Ru(1)–Cl(2)	175.55(3)
Ru(1)–N(1)	2.074(2)	N(1)–Ru(1)–N(2)	79.12(9)
Ru(1)–N(4)	2.052(2)	N(4)–Ru(1)–N(2)	78.59(9)
Ru(1)–N(5)	1.761(2)	N(4)–Ru(1)– Cl (1)	88.88(7)
N(5)–O(2)	1.147(3)	N(4)–Ru(1)– Cl (2)	90.14(7)
		O(2)–N(5)–Ru(1)	169.4(2)
4			
Ru(1)–Cl(1)	2.3858(12)	N(3)–Ru(1)–N(2)	77.71(15)
Ru(1)–P(1)	2.4057(13)	N(1)–Ru(1)–N(4)	96.44(16)
Ru(1)–N(4)	2.082(3)	P(1)–Ru(1)–Cl(1)	173.71(5)
Ru(1)–N(3)	2.002(4)	N(4)–Ru(1)–N(3)	78.17(15)
Ru(1)–N(2)	2.077(3)	N(4)–Ru(1)–N(2)	155.39(14)
Ru(1)–N(1)	1.731(4)	N(2)–Ru(1)–P(1)	92.53(9)
N(1)–O(1)	1.142(4)	N(1)–Ru(1)–P(1)	89.88(12)
		O(1)–N(1)–Ru(1)	173.7(4)

The UV-Vis spectra of **1** and **4** were displayed in Fig. S8.‡ A charge transfer band with λ_{max} near 425 nm was found in the spectrum of complex **4** while in case of **1**, two bands were found near 383 nm and 442 nm. Complexes **1** and **4** exhibited one strong absorption band near 274 nm and 302 nm respectively.

The N–O stretching frequencies (ν_{NO}) in the IR spectra of **1** and **4** were observed around 1870 cm^{-1} and 1890 cm^{-1} respectively, expected for $\{Ru–NO\}^6$ type of complexes[2–5] (Fig. S9 and S10‡). The ν_{NO} value for **1** was lesser than the value found in **4** probably due to the presence of strong σ-donating carboxamido nitrogen *trans* to NO in complex **1**.[24,25] Moreover, the Ru–N–O angles are 169.4° and 173.7° respectively for complexes **1** and **4**. Hence in **4**, the Ru–N–O moiety is more linear and provided a higher NO stretching frequency. These data were consistent with the Ru–N and N–O distances[24,25] in complexes **1** and **4**. In fact we found that both the distances are smaller in case of **4** compared to the same for **1** which implied the better overlap of NO with metal in **4**. A peak at ~1650 cm^{-1} was observed in the IR spectrum of **1** due to the presence of the –CONH– group.[11]

Photolysis experiments

Photolability of the coordinated NO was studied by exposing solutions of nitrosyl complexes **1** and **4** under visible as well as UV light. Upon exposure to visible light (100 W tungsten lamp), the solutions of the nitrosyl complexes did not afford many changes in the UV-Vis spectra. However rapid spectral changes were observed when the solutions were exposed to low intensity light of the UV lamp (λ_{max} = 365 nm). This indicated that complexes are more efficient in terms of NO donation under UV light.[2a,b]

Exposure of an acetonitrile solution of **1** to low intensity UV light (λ_{max} = 365 nm) resulted in rapid loss of NO (Fig. 3(a)) with the formation of a new peak at 450 nm. Similarly, illumination of UV light (λ_{max} = 365 nm) through an acetonitrile

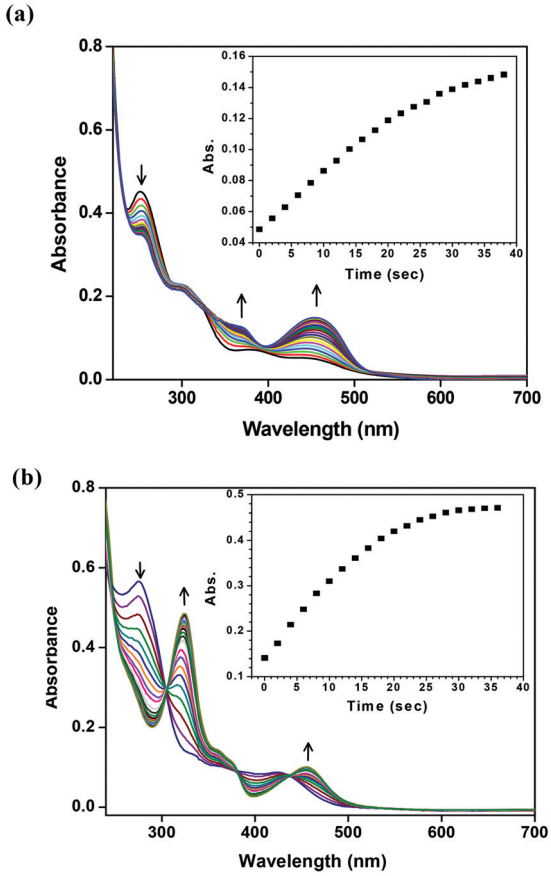


Fig. 3 Photocleavage of NO from complexes (a) **1** (~2.1 × 10^{-5} M) and (b) **4** (~2.0 × 10^{-5} M) in acetonitrile solution under illumination of a low intensity UV lamp (λ_{max} = 365 nm). Repetitive scans were taken in 2 s intervals. Inset: time dependent changes in absorbance at λ = 456 nm and λ = 325 nm for **1** and **4** respectively.

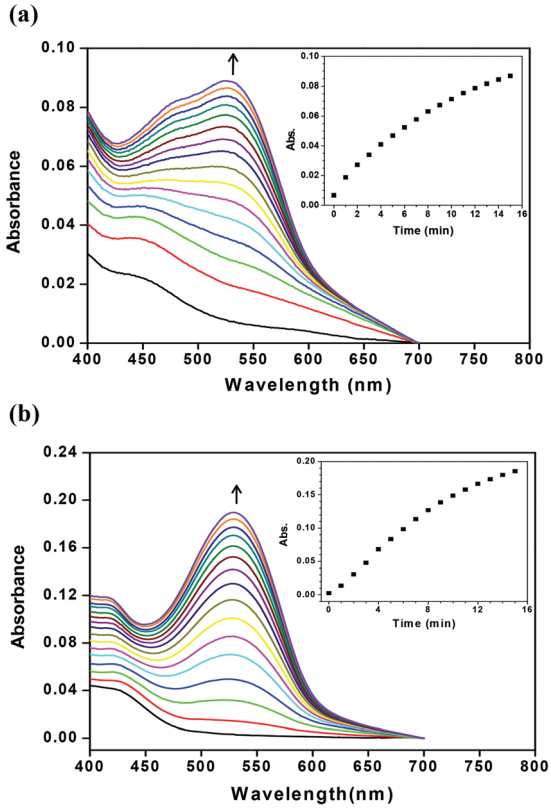


Fig. 4 Electronic spectra of the formation of dye when Griess reagent (100 μL) was treated with complexes (a) **1** (10^{-4} M) and (b) **4** (10^{-4} M) in the presence of the light of a UV lamp (λ_{irr} = 365 nm). Repetitive scans were taken in 1 minute intervals. Inset: time dependent changes in absorbance with λ_{max} near 538 nm.

solution of complex **4** (Fig. 3(b)) afforded spectral changes along with the appearance of new absorption peaks near 322 nm and 455 nm. There was no loss of NO in dark conditions. The presence of clear isosbestic points in electronic spectra showed the formation of clean photoproducts. The quantum yield (ϕ) values by chemical actinometry[5a] for NO photorelease from complexes **1** and **4** (λ_{irr} = 365 nm) were found to be 0.002 ± 0.001 and 0.003 ± 0.001 respectively in acetonitrile solutions.

Griess reaction to estimate the photoreleased NO

By using a Griess reagent assay,[5a] we estimated the amount of photoreleased NO from nitrosyl complexes. The presence of photolabile NO in complexes **1** and **4** was further confirmed by observing the increase in optical density of the produced dye at ~538 nm in ultraviolet light. In dark conditions, a negligible amount of NO was found to be released. In the Griess reaction, exposure of UV light for 15 minutes to 100 μM solutions of both the complexes **1** and **4** gave rise to ~2 μM and ~5 μM (Fig. 4 and Table 3) of dye formation respectively.

The change in absorbance of azo dye produced from Griess reagent was found to be very small under visible light (100 W tungsten lamp). The results of estimated NO from our nitrosyl complexes were compared with the data obtained from sodium nitroprusside (SNP), a well known NO donor drug[2b,d,26] under the same experimental conditions. In ultraviolet light, a 100 μM solution of SNP provided ~6.0 μM of nitric oxide (Table 3).

These data afforded the formation of NO in solution and the concentration of photoreleased NO in **4** was close to the amount of NO released by SNP however in case of **1** the photorelease of NO was very less.

Table 3 Estimation of NO production from **1**, **4** and sodium nitroprusside (SNP) in Griess reagent assay and DPPH quenching experiment

		NO produced[a] (μM)		Reactive species produced[a] (μM)	
		Griess reaction		DPPH quenching	
Complex	Complex conc.	Dark	UV light	Dark	UV light
1	100 μM	0.005	2.0	0.23	5.3
4	100 μM	0.004	4.6	0.28	6.0
SNP	100 μM	0.040	5.7	—	—[b]

[a] Average of three experiments. [b] Data is not provided due to solubility constraints.

Trapping of NO by reduced myoglobin

The photoreleased NO from the nitrosyl complexes was transferred to the heme iron center of reduced myoglobin using low intensity light of a UV lamp. Electronic absorption spectra were obtained in phosphate buffer (pH ~ 6.8). The absorption spectra for oxidized myoglobin (Mb) showed an intense band at ~409 nm (Soret band). The UV-Vis spectra of reduced myoglobin near 433 nm was obtained by the addition of excess sodium dithionite to the same cuvette. When acetonitrile solutions of complexes were added to buffer solutions of reduced myoglobin under dark conditions, no reaction was observed. However when the same mixtures were exposed to a UV lamp (λ = 365 nm) for 2–3 minutes, the absorption spectra near 422 nm (for **1**, Fig. S11‡) and 424 nm (for **4**) showed the formation of myoglobin-NO adducts.[5]

DPPH radical scavenging assay

DPPH (2,2-diphenyl-1-picrylhydrazine) radical is often used for the determination of antioxidant properties of different compounds, foods *etc.*[16–19] During this estimation, the intense violet colour of the DPPH radical disappears and with UV-Vis spectroscopic data, antioxidant properties are quantified. It has been observed that quenching of the radical was responsible for the disappearance of this violet colour of DPPH radical. This prompted us to examine the disappearance of the violet colour of DPPH in the presence of a photolabile NO radical derived from complexes **1** and **4**, keeping in mind that NO itself as well as other generated radicals could decolourise DPPH. Acetonitrile solution of complex **1** was exposed to UV light in the presence of the DPPH radical and we expected that NO as well as other reactive nitrogen or oxygen species could quench the DPPH radical. Interestingly, a decrease in the absorbance of DPPH near 520 nm was observed (Fig. S12‡). We have estimated the amount of reactive species generated due to the photorelease of NO from **1** and **4** by monitoring the absorbance of DPPH near 520 nm and the results are described in Table 3.

The values obtained from DPPH quenching studies are slightly higher than of the data obtained from Griess reaction. This was probably due to the formation of other reactive species in DPPH solution under aerobic conditions.

Cyclic voltammetric studies

Electrochemical studies were performed to examine the redox properties of **1**, **2** and **4** in dichloromethane solutions (Fig. 5). In the case of complex **1**, we did not observe any redox couple and we found only one cathodic peak near E_{ca} = −0.64 V *vs.* Ag/AgCl. This data was not promising for our strategy of synthesizing a ruthenium nitrosyl complex having $\{RuNO\}^5$ species because of the absence of our expected $\{RuNO\}^6$/$\{RuNO\}^5$ redox couple.

The cyclic voltammogram of **2** showed a quasireversible redox couple with an $E_{1/2}$ value near +0.80 V *vs.* Ag/AgCl which was assigned to the Ru(II)/Ru(III) couple[4d,5a] (Fig. 5, dashed line). Interestingly, we found a quasireversible redox couple for

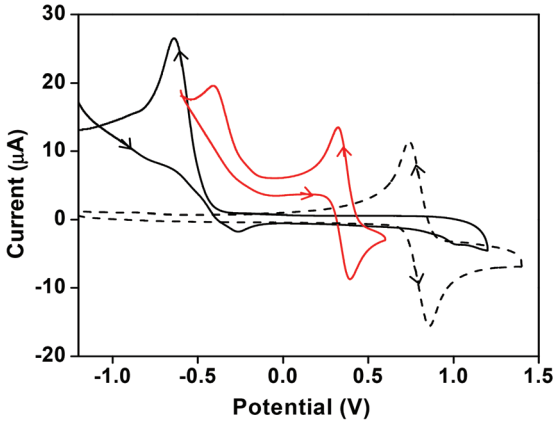


Fig. 5 Cyclic voltammograms of a 10^{-3} M solutions of complexes **1** (black solid line), **2** (dashed line) and **4** (red line) in dichloromethane solutions in presence of 0.1 M tetrabutylammonium perchlorate (TBAP) using working electrode: glassy-carbon; reference electrode: Ag/AgCl; auxiliary electrode: platinum wire; scan rate 0.1 V s^{-1}.

4 which afforded the $E_{1/2}$ value of +0.36 V *vs.* Ag/AgCl (Fig. 5, red line). Hence we found a less positive (~450 mV) $E_{1/2}$ value of complex **4** as compared to **2**. These results prompted us to investigate the oxidation of **4** (rather than **1**) and isolation of the resultant complex which would be our desired nitrosyl complex having the $\{RuNO\}^5$ moiety. We would like to mention here that we found a cathodic peak near −0.40 V *vs.* Ag/AgCl which indicated that the reduction of **4** to generate a complex containing $\{RuNO\}^7$ moiety was not feasible in our complex.

Formation of complex $[Ru(L^2)(PPh_3)(NO)Cl](NO_3)_3$ (5) having $\{RuNO\}^5$ moiety

The formation of **5** was observed by chemical oxidation of $[Ru(L^2)(PPh_3)(NO)Cl](ClO_4)_2$ (**4**) with ceric ammonium nitrate (CAN, in excess) in acetonitrile solution.[27] Complex **5** was soluble in acetonitrile, methanol and dimethylformamide however it is important to note here that **5** was found to be unstable in methanol and dimethylformamide. UV-Vis and IR spectral studies clearly indicated the formation of complex **5** (Fig. S13‡). The IR spectrum of **5** (Fig. S14‡) gave rise to a ν_{NO} value near 1910 cm^{-1} and this band went back to 1890 cm^{-1} upon reduction with sodium dithionite. These data showed that the oxidation afforded only a 20 cm^{-1} change in ν_{NO} value on going from **4** to **5**. A new peak near 1390 cm^{-1} also appeared in the IR spectrum of **5**, probably due to the presence of counter anion NO_3^- (shown in Fig. S14‡).

The description of the $\{Ru–NO\}^6$ moiety in **4** as $\{Ru^{II}–NO^+\}^6$ prompted us to speculate a metal centered oxidation of **4** and we performed EPR spectral studies on complex $[Ru(L^2)(PPh_3)(NO)Cl](NO_3)_3$ (**5**) (*vide infra*). The electronic spectrum of complex **4** afforded a peak near 425 nm which was characteristic of the complex. This peak was not observed after the addition of CAN (Fig. S13(b)‡) to the same solution. Interestingly we got back an electronic spectrum similar to **4** when sodium dithionite (2 mM) was added to the cuvette containing complex **4** after chemical oxidation by CAN.

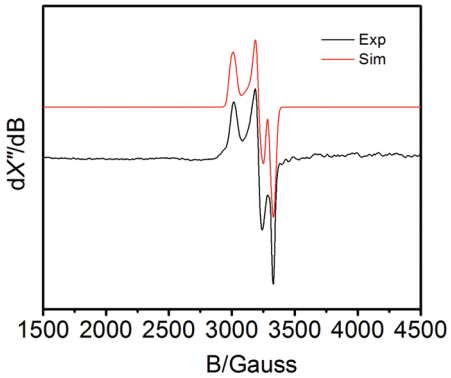


Fig. 6 The solid state EPR spectrum of complex **5** at 77 K with experimental (black) and simulated (red) spectral lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

Table 4 Comparison of *g* values of complex **5** with the *g* values reported by Kaim and coworkers[10]

Complex	g_1	g_2	g_3	g_{av}
$[Cl_5Ru(NO)]^-$	2.11	2.11	2.058	2.091[10]
Complex **5**	2.165	2.032	1.961	2.053

We mentioned earlier that the $\{Ru–NO\}^6$ moiety in **4** could be described by $\{Ru^{II}–NO^+\}^6$. Oxidation of **4** may lead to the formation of new complex having $\{RuNO\}^5$ species where the oxidation could be either metal centered ($\{Ru^{III}NO^+\}^5$) or ligand centered ($\{Ru^{II}NO^{++}\}^5$) and this could easily be found out by performing EPR spectral studies on complex **5**.

The EPR spectrum of **4** after the addition of CAN was recorded in solid state at 77 K and is displayed in Fig. 6. The spectrum observed in this study clearly depicted the formation of a $\{Ru^{III}–NO^+\}^5$ moiety. The *g* values found in the study were consistent with values reported by Kaim and coworkers[10] (Table 4).

The geometry optimisation for complexes **1** and **4** was performed at the B3LYP level[20,21] of DFT using LANL2DZ basis set[21] for ruthenium metal. The optimised structures of nitrosyl complexes showed nearly linear geometries for the $\{RuNO\}^6$ moiety and provided ~172° for the Ru–N–O angle (Table S2‡). The N–O bond distances (~1.19 Å in **1** and ~1.18 Å in **4**) as well as ν_{NO} values (1837 cm^{-1} for **1** and 1886 cm^{-1} for **4**) supported the $\{Ru^{II}–NO^+\}^6$ description of the $\{RuNO\}^6$ moiety in the optimised structures (scaling factor was 0.97).[22]

The highest occupied molecular orbital (HOMO) of complex **1** was found to be located over the ligand (L^1) along with minor contributions from the metal centre and the ligand NO. However structure optimisation of **4** afforded no contribution of NO in the HOMO of **4** (Fig. 7 and Table S3‡). These results were consistent with the IR data of **5** where we found only a change of ~20 cm^{-1}. We would like to mention here that the complex $[Mn(PaPy_3)(NO)](ClO_4)$ reported by Mascharak and coworkers[27] gave rise to similar oxidation and the change in ν_{NO} was ~130 cm^{-1}. These data clearly indicated

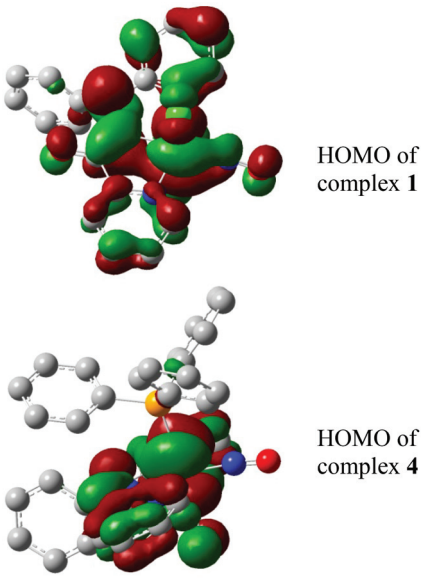


Fig. 7 Highest occupied molecular orbitals (HOMOs) of nitrosyl complexes **1** and **4**.

that during the $\{MnNO\}^6$ to $\{MnNO\}^5$ conversion *via* oxidation, the involvement of non-innocent ligand NO was significant. However, in our case, a very small involvement of NO and a significant contribution from the L^2 and metal centre was proposed.

The time dependent DFT (TD-DFT) calculations were also performed to evaluate electronic absorption spectra of **1** and **4** (Fig. S15‡). The bands appearing in the computed spectra were found to be closely related to those of experimental spectra. The information obtained from the calculated electronic transitions, excitation energies (in eV), and oscillator strengths (*f*) was displayed in Table S4.‡ In the case of complex **1**, the absorption peak calculated at 449 nm was slightly red shifted to the experimental band (at 442 nm) and probably arose from HOMO → LUMO + 2 transitions. A band near 348 nm was blue shifted with respect to experimental value and appears to be a composition of three main transitions dominated by HOMO → LUMO + 5, HOMO − 12 → LUMO + 1 and HOMO − 1 → LUMO + 6 excitations. In complex **4**, the absorption peak near 420 nm was close to the experimental value and was observed due to the presence of a HOMO → LUMO + 2 transition.

Conclusions

In conclusion, we have synthesized and characterized complexes **1**, **2**, **3** and **4** and molecular structures of nitrosyl complexes **1** and **4** were determined by X-ray crystallography. Both the nitrosyl complexes **1** and **4** having $\{RuNO\}^6$ species afforded free NO upon illumination of light. Photorelease of NO was authenticated by transferring NO to reduced myoglobin and liberated NO was estimated by Griess reaction. Generation of reactive oxygen and/or reactive nitrogen species was investigated by DPPH radical quenching assay. Redox

properties of complexes were examined by cyclic voltammetric studies and complex **4** afforded a redox couple near +0.36 V *vs.* Ag/AgCl. Complex **4** afforded **5** upon chemical oxidation with ceric ammonium nitrate. Complex **5** was found to be a rare example of a ruthenium nitrosyl complex having a $\{RuNO\}^5$ moiety and was characterized by UV-Vis, IR and EPR spectral studies. The results of this study supported a $\{Ru^{III}NO^{+}\}^5$ description of the $\{RuNO\}^5$ moiety and to some extent an innocent behaviour of non-innocent ligand NO was observed during the chemical oxidation of **4**. Complex **4** was regenerated from **5** after chemical reduction by sodium dithionite. To the best of our knowledge, this is the first report of isolation and characterization of ruthenium nitrosyl complex having a $\{RuNO\}^5$ species.[10] Further works on related complexes and applications of nitrosyl complexes are in progress.

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