Supporting Information

For

Visible Light Induced Reversible Extrusion of Nitric Oxide from a Ruthenium(II) Nitrosyl Complex: a Facile Delivery of Nitric Oxide

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The red solution of **1** (0.10 g, 0.12 mmol) methanol (15 mL) was irradiated with visible light (Osram tungsten halogen lamp 100 W, cut-off filter $\lambda \geq 455$ nm) at 20 °C for 135 min. The solution color changed gradually to green, and the reaction was monitored by IR spectroscopy. IR spectral changes are shown in Figure 1S.

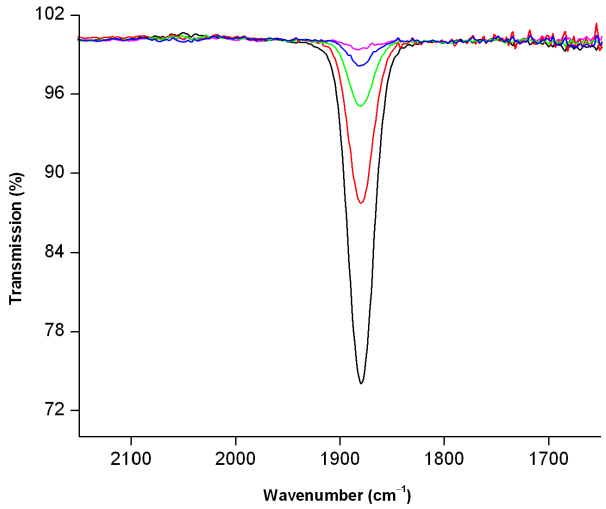

Figure 1S. IR spectra of **1** in MeOH during visible light irradiation ($\lambda \geq 455$ nm); t = 0 (black), 30 (red), 60 (green), 120 (blue) and 135 min (violet).

The green microcrystals of [Ru(Br)(py^{bu}S$_4$)] (**1a**) were filtered, washed with Et_2O and dried. Yield: 50 mg (50%). Elemental analysis calcd.(%) for $C_{35}H_{48}NS_4RuBr$: C 53.14, H 6.12, N 1.77, S 16.22; found: C 53.33, H 6.59, N 1.73, S 16.16. MS (FD, CH_2Cl_2): m/z = 791 [M^+]. CV (THF, vs NHE): –0.62 V (**1a**$^{0/-1}$); 0.44 V (**1a**$^{0/+1}$).

When a suspension of **1a** (0.09 g, 0.12 mmol) in MeOH (15 mL) was stirred with 5 equiv of NO at 20 °C for 16 h. The green suspension changed to a red solution. Figure 2S depicts the IR spectrum of the red solution, which confirms the reappearance of the NO band of **1**. In addition, some other NO species were formed

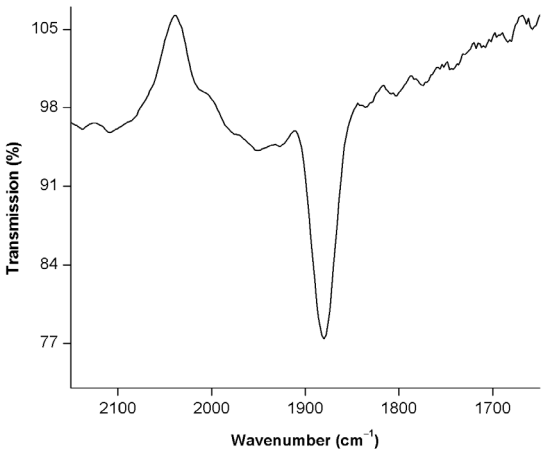

Figure 2S. IR spectrum of the red solution formed during the treatment of **1a** with NO (5 equiv) in MeOH after 16 h.

Figure 3S

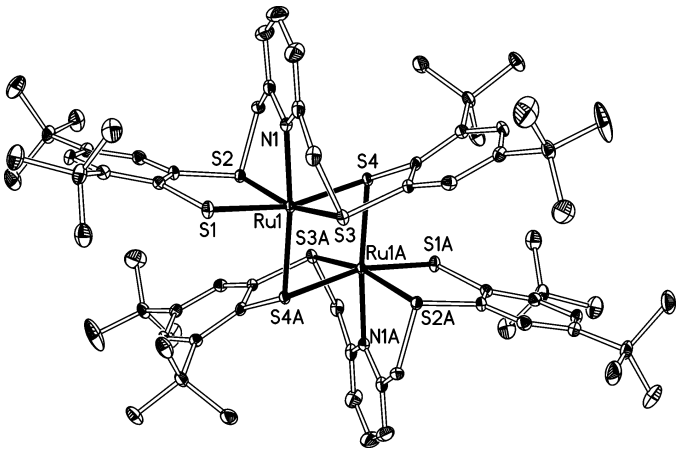

Figure 3S. ORTEP diagram of the dication **1b** (50% probability ellipsoids; H atoms and solvent molecules omitted). Selected distances [Å] and angles [°]: Ru–N1 2.102(2), Ru1–S1 2.3520(6), Ru1–S2 2.3397(5), Ru1–S3 2.3374(5), Ru1–S4 2.3338(5), Ru1–S4A 2.3219(6), Ru1···Ru2 2.8087(4), S1–Ru1–N1 80.40(5), S1–Ru1–S2 86.61(2), S1–Ru1–S3 90.4(2), S1–Ru1–S4 164.01(2), S1–Ru1–S4A 90.11(2), S2–Ru1–S3 166.16(2), S2–Ru1–S4 92.09(2), S2–Ru1–S4A 100.03(2), S2–Ru1–N1 83.23(5), N1–Ru1–S4A 169.80(5), Ru1–S4–Ru2 74.21(2).

Elemental analysis calcd.(%) for **1b** C 53.15, H 5.99, N 1.77, S 16.21; found: C 53.35, H 6.05, N 1.74, S 15.90. CV (THF, vs NHE): –280 V (**1b**$^{2+/1+}$); –674 V (**1b**$^{1+/0}$).

Figure 4S

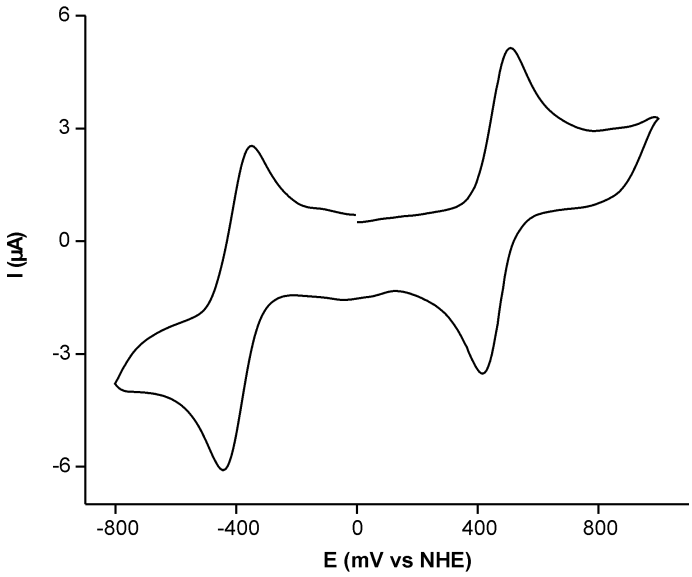

Figure 4S. Cyclic voltammogram of **3** in DMF (10^{-3} M; NBu_4PF_6, 10^{-1} M; scan speed, 100 mV s^{-1}) at 20 °C.

Figure 5S

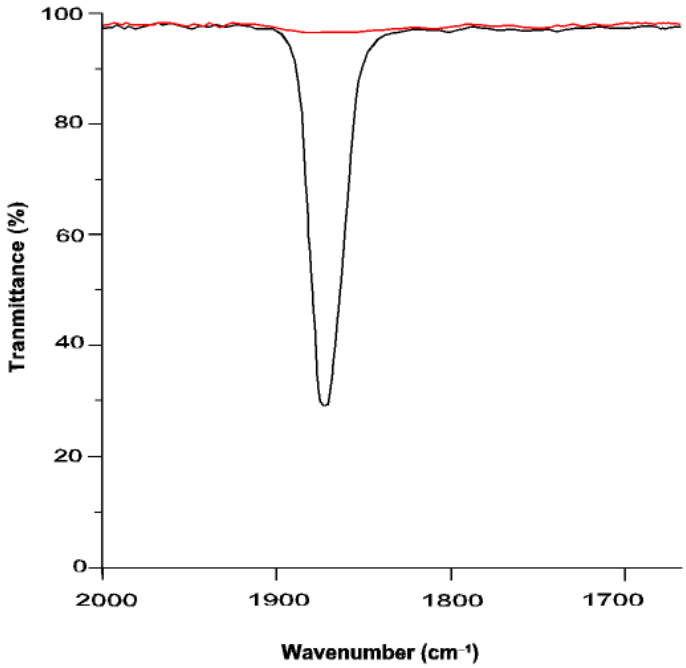

Figure 5S. IR spectra of **3** in MeOH during UV light irradiation (Osram XBO 150 W Xenon arc lamp; Cut-Off filter $\lambda \geq$ 320 nm); t = 0 (black) and 5 min (red).

Table 1S . Spectroscopic, electrochemical and x-ray structural data of **3** and **1**.

Techniques		**3**	**1**
IR	a) KBr.	1858 cm^{-1}	1842 cm^{-1}
	b) MeOH	1872 cm^{-1}	1879 cm^{-1}
UV-visible (MeOH)		λ 251 nm, ε 43.2×10^3 mol^{-1} cm^{-1}	λ 246 nm, ε 27.2×10^3 mol^{-1} cm^{-1}
		λ 283 nm, ε 23.2×10^3 mol^{-1} cm^{-1}	λ 280 nm, ε 14.8×10^3 mol^{-1} cm^{-1}
		λ 334 nm, ε 7.8×10^3 mol^{-1} cm^{-1}	λ 325 nm, ε 5.7×10^3 mol^{-1} cm^{-1}
		λ 471 nm, ε 0.9×10^3 mol^{-1} cm^{-1}	λ 460 nm, ε 0.7×10^3 mol^{-1} cm^{-1}
CV (DMF, vs NHE)		0.46 V	0.52 V
		–0.38 V	–0.32 V
X-ray	Ru–N(O)	1.748(4) Å	1.721(6) Å
	Ru–N(py)	2.099(4) Å	2.107(5) Å
	N–O	1.144(5) Å	1.156(6) Å
	Ru–N–O	178.8(4)°	178.1(6)°

Experimental Section

Synthetic reactions were carried out in dry and degassed solvents using standard Schlenk techniques. Physical measurements were performed with the following instruments: IR (KBr discs or CaF_2 cuvettes, solvent bands were compensated), Perkin-Elmer 983, 1620 FT-IR and 16PC FT-IR; Uv-vis: UV-3101PC UV-vis-NIR; NMR: Jeol JNM-GX 270, Jeol JNM-EX 270, and Lambda LA 400 with the residual signals of the deuterated solvent used as an internal reference. Chemical shifts are quoted in the δ scale (downfield shifts are positive). Mass spectra: Jeol MSTATION 700 spectrometer. Elemental analysis: Carlo Erba EA 1106 or 1108 analyzer. Cyclic voltammetry (CV): EG&G potentiostat PAR model 264A and a conventional three electrode assembly consisting of a glassy carbon working electrode and Pt reference and counter electrodes. Solutions: DMF/THF [10^{-3} M]; supporting electrolyte: Bu_4NPF_6 [10^{-1} M]; internal standard: ferrocene, $E(F_c/F_c^+)$ = +0.41 V vs. NHE;[1] scan speed: 100 mV s^{-1}: T = 20 °C. The reversibility of the voltammograms and the number of electrons involved in the redox processes were determined as described in the literature.[2] 2,6-bis(bromomethyl)pyridine and compound **1** were prepared according to the reported method.[3]

Irradiation reaction. The irradiation reaction was carried out in a jacketed cylindrical quartz cuvette (capacity 15 mL) attached to an optical train. Irradiation was performed with an Osram tungsten halogen lamp 100 W installed in Amko lamp-housing unit 02-A1100 equipped with an Amko DC power supply DF-3010-A. For visible light irradiation reaction, a cut-off filter of λ ≥ 455 nm was placed in front of the cuvette. For UV light irradiation reaction, Osram XBO 150 W Xenon arc lamp installed in a light condensing lamp-housing unit PTI, A1010S and a cut-off filter of λ ≥ 320 nm were used.

Synthesis of 3-triphenylsilyl-1,2-benzenedithiol ($^{si}S_2$-H_2). To the suspension of benzenedithiol (6.7 g, 47.1 mmol) in hexane (150 mL), *n*BuLi (2.5 M in hexane, 83 mL, 207.5 mmol) and TMEDA (31.5 mL, 210.0 mmol) were added at –78 °C, and was allowed to stir for 4 d at 20 °C. The color of the suspension changed from white to pale yellow. To this, Ph_3SiCl (56.7 g, 192.3 mmol) in THF (50 mL) was added at –78 °C, and was continued to stir for 24 h at 20 °C. The resulting white suspension was acidified with HCl (10%, pH < 2) at 0 °C and extracted with Et_2O (2 × 250 mL). Further work-up of the Et_2O phase, according to our earlier report,[4] yielded a white residue. This was refluxed in MeOH (150 mL) for 15 h. The residue was filtered, and was dissolved in NaOMe (50 mL) to remove some insoluble materials. The filtrate was treated with conc. HCl (pH < 2). The white precipitate formed were filtered and washed with H_2O and MeOH, and dried. Recrystallized with CH_2Cl_2/Et_2O. Yield: 12.1 g (64%). Elemental analysis calcd (%) for $C_{24}H_{20}S_2Si$: C 71.95, H 5.03, S 16.01; found C 71.92, H 5.19, S 15.82. ^{1}H NMR (269.7 MHz, $CDCl_3$): δ = 7.60-6.95 (m, 18 H; C_6H_3/C_6H_5), 3.83 (s, 1 H; SH), 3.65 (s, 1 H; SH); $^{13}C\{^1H\}$ NMR (67.8 MHz, $CDCl_3$): δ = 137.6, 137.1, 136.9, 136.3, 134.2, 133.9, 132.2, 129.7, 128.0, 126.3 (C_6H_3/C_6H_5); IR (KBr): $\tilde{\nu}$ = 2531 cm^{-1} ν(SH); MS (FD, THF): *m/z*(%): 400 (100) [M^+].

Synthesis of $Bu_4N[Ru(NO)(^{si}S_2)_2]$, 2. NO gas was bubbled into a red solution of $RuCl_3{\cdot}xH_2O$ (1.6 g, 6.1 mmol) in MeOH for 3 h, then stirred under NO for 15 h. Removal of the solvent resulted in a dark-red oil. It was dissolved in THF (30 mL), and cooled to –78 °C. To this, $^{si}S_2$-H_2 (5.0 g, 12.5 mmol) and *n*BuLi (2.5 M solution in hexane, 10.3 mL, 25.7 mmol) in THF (15 mL) was added. After stirring for 2 h at 20 °C, the solvent was removed. The residue was dissolved in MeOH (30 mL), and treated with Bu_4NBr (2.2 g, 6.7 mmol) in MeOH (15 mL) to give green microcrystals of **2**. Yield: 4.9 g (70%). Elemental analysis calcd.(%) for **2** ($C_{64}H_{72}N_2OS_4Si_2Ru$): C 65.66, H 6.20, N 2.39, S 10.96; found C 65.46, H 6.57, N 2.32, S 10.93; ^{1}H NMR (269.7 MHz, DMSO[D_6]): δ = 7.61-6.74 (m, 36 H, C_6H_3/C_6H_5), 3.14 (m, 8 H; Bu_4N), 1.54 (m, 8 H; Bu_4N), 1.28 (m, 8 H; Bu_4N), 0.91 (t, 12 H; Bu_4N); ^{13}C NMR (67.8 MHz, DMSO[D_6]): δ = 158.4, 151.4, 135.9, 134.9, 132.9, 132.4, 130.5, 129.2, 127.6, 122.1 (C_6H_3/C_6H_5), 57.5, 23.0, 19.2, 13.5(Bu_4N); IR(KBr): $\tilde{\nu}$ = 1728 cm^{-1} ν(NO).

Synthesis of $[Ru(NO)(py^{si}S_4)]Br{\cdot}THF$, 3·THF. To a refluxing solution of **2** (4.7 g, 4.1 mmol) in THF (150 mL), 2,6-bis(bromomethyl)pyridine (1.5 g, 5.8 mmol) in THF (20 mL) was added slowly, and was allowed to reflux for another 5 h. The violet microcrystals of **3**·THF formed were filtered, washed with THF (70 mL) and dried in vacuo. Yield: 3.4 g (71%). Elemental analysis calcd.(%) for **3**·THF ($C_{59}H_{51}N_2O_2S_4Si_2BrRu$): C 59.77, H 4.34, N 2.36, S 10.82; found C 59.56, H 4.49, N 2.40, S 10.51; ^{1}H NMR(269.7 MHz, DMSO[D_6]): δ = 8.06 (d, 2 H, C_5H_3N), 8.00 (t, 1 H, C_5H_3N) 7.67 (d, 2 H, C_6H_3), 7.50-7.15 (m, 32 H, C_6H_5/C_6H_3), 7.01 (d, 2 H, C_6H_3), 4.95 (d, 2 H, CH_2), 4.04 (d, 2 H, CH_2), 3.58 (s, 4 H, C_4H_8O), 1.74 (s, 4 H, C_4H_8O); ^{13}C NMR (67.8 MHz, DMSO[D_6]): δ = 157.5, 156.5, 140.2, 140.0, 135.8, 135.2, 135.0, 133.7, 129.8, 129.5, 128.2, 125.0, 124.7 ($C_5H_3N/C_6H_3/C_6H_5$), 67.2 (C_4H_8O), 55.0 (CH_2), 25.3 (C_4H_8O); IR(KBr): $\tilde{\nu}$ = 1858 cm^{-1} ν(NO); MS(FD, DMF): *m/z*(%): 1033 (100) [$Ru(NO)(py^{si}S_4)^+$].

Conversion of 3 to [Ru(Br)(py^{si}S$_4$)] (4) by visible light irradiation. A red solution of **3** (0.6 g, 0.5 mmol) in MeOH (15 mL) was irradiated (λ ≥ 455 nm) in a cylindrical cuvette at 20 °C for 30 min, and the reaction was monitored by IR spectroscopy. The solution color changed to green, and subsequently green microcrystals were precipitated. The precipitate was filtered, washed with MeOH (10 mL) and dried in vacuo. Yield: 0.5 g (92%). Crystals of **4** suitable for X-ray structure analysis were obtained from THF/DMF (1:2) mixture was kept at –20 °C for 4 d. Elemental analysis calcd. (%) for **4** ($C_{55}H_{43}NS_4Si_2BrRu$): C 60.98, H 4.00, N 1.29, S 11.84; found C 61.08, H 3.87, N 1.26, S 11.56; MS (FAB, NBA): *m/z*(%): 1083 (100) [Ru(Br)(py^{si}S$_4$)$^+$].

Conversion of 3 to 4 by UV light irradiation. As above, except with λ ≥ 320 nm cut-off filter; irradiation time, 5 min. Yield: 0.46 g (86%).

Conversion of 4 to 3. The green suspension from the visible light irradiation reaction was stirred under an atmosphere of NO for about 60 min. The suspension was changed to red solution. IR spectrum of the solution showed that the NO band of **3** reappeared with almost identical intensity as shown in Figure 2a. This solution was filtered, concentrated to 1 mL, and treated with THF (30 mL) to get a purple red powder of **3**. Yield: 0.54 g (90%).

X-ray structural analysis of 1b·4MeOH, 2·MeOH, 3·CH$_2$Cl$_2$·MeCN and 4·2DMF. Suitable single crystals were embedded in protective perfluoro polyether oil. Data were collected at T = 100 K on a Bruker-Nonius KappaCCD diffractometer using MoK_α radiation (λ = 71.073 pm), and a graphite monochromator. A semi-empirical absorption correction based on multiple scans (SADABS[5]) was performed for **1b**·4MeOH, **2**·MeOH, **3**·CH_2Cl_2·MeCN and **4**·2DMF. The structures were solved by direct methods, full-matrix least-squares refinement was carried out on F^2 using SHELXTL NT 6.12.[6] All non-hydrogen atoms were refined anisotropically. All H-atoms were geometrically positioned with isotropic displacement parameters being 1.5 U(eq) of the proceeding C or N atom. Two MeOH molecules in **1b** are disordered, and two alternative sites have been refined to give occupancies of 71.9(6) and 28.1(6)%. The CH_2Cl_2 molecule in **3** is disordered, and two alternative sites have been refined to give occupancies of 63.7(6) and 36.3(6)%, respectively. The two DMF molecules in **4** are disordered, and two alternative sites have been refined to give occupancies of 64.5(5) and 35.5(5)%. Selected crystallographic data for **1b**: $C_{74}H_{110}Br_2N_2O_4Ru_2S_8$, crystal size 0.16×0.12×0.04 mm, triclinic, space group P1 bar, a = 10.9433(7), b = 13.835(1), c = 14.3122(8) Å, α = 72.949(5), β = 78.142(4), γ = 75.680(5)°, V = 1986.5(2) Å^3, Z = 1, ρ_{calcd} = 1.430 Mg m^{-3}, μ = 1.642 mm^{-1}, (6.0<2θ<56.0°), $T_{min/max}$ = 0.838/1.000, 49974 measured reflections, 9554 unique reflections, 7585 observed reflections [I>2σ(I)], 448 parameters, R1 = 0.0291 [I>2σ(I)], wR2 = 0.0586 (all data). **2**: $C_{65}H_{76}N_2O_2RuS_4Si_2$, crystal size 0.16×0.09×0.05 mm, triclinic, space group P1, a = 9.4625(8), b = 9.9173(7), c = 16.7418(8) Å, α = 99.580(5), β = 92.874(5), γ = 101.063(6)°, V = 1514.9(2) Å^3, Z = 1, ρ_{calcd} = 1.318 Mg m^{-3}, μ = 0.481 mm^{-1}, (6.7<2θ<52.8°), $T_{min/max}$ = 0.944/1.000, 18582 measured reflections, 10522

unique reflections, 7534 observed reflections [$I>2\sigma(I)$], 688 parameters, $R1$ = 0.0597 [$I>2\sigma(I)$], w$R2$ = 0.1242 (all data). **3**: $C_{58}H_{48}BrCl_2N_3ORuS_4Si_2$, crystal size 0.41×0.34×0.34 mm, monoclinic, space group $P2_1/n$, a = 11.3865(2), b = 28.6040(5), c = 1716.45(3) Å, α = 90.0, β = 92.782(2), γ = 90.0°, V = 5583.9(2) Å^3, Z = 4, ρ_{calcd} = 1.474 Mg m^{-3}, μ = 1.328 mm^{-1}, (7.3<2θ<52.8°), $T_{min/max}$= 0.865/1.000, 34673 measured reflections, 10772 unique reflections, 7733 observed reflections [$I>2\sigma(I)$], 678 parameters, $R1$ = 0.0554 [$I>2\sigma(I)$], $wR2$ = 0.1126 (all data). **4**: $C_{61}H_{57}BrN_3O_2RuS_4Si_2$, crystal size 0.52×0.22×0.15 mm, monoclinic, space group $C2/c$, a = 19.8857(4), b = 10.9211(2), c = 26.5136(5) Å, α = 90, β = 98.956(1), γ = 90°, V = 5687.9(2) Å^3, Z = 4, ρ_{calcd} = 1.436 Mg m^{-3}, μ = 1.213 mm^{-1}, (6.9<2θ<60.0°), $T_{min/max}$= 0.818/1.000, 37129 measured reflections, 8113 unique reflections, 5591 observed reflections [$I>2\sigma(I)$], 368 parameters, $R1$ = 0.0444 [$I>2\sigma(I)$], $wR2$ = 0.0897 (all data). CCDC 273824 (**1b**), CCDC 255034 (**2**), CCDC 255035 (**3**) and CCDC 273825 (**4**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (44)1223-336-033; or deposit@ccdc.cam.ac.uk).

References

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