Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information:

Synthetic NO reduction cycle on a bis(pyrazolato)-bridged dinuclear ruthenium complex including photo-induced transformation

Yasuhiro Arikawa,* Junko Hiura, Chika Tsuchii, Mika Kodama, Naoki Matsumoto, and Keisuke Umakoshi

Division of Chemistry and Materials Science, Graduate School of Engineering, Nagasaki University, Bunkyo-machi 1-14, Nagasaki 852-8521, Japan.

Experimental Procedures

General Procedures: All reactions were carried out under N_2 or Ar unless otherwise noted and subsequent work-up manipulations were performed in air. The starting material $[(TpRu)_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)]$ (**1**) was prepared according to the previously reported method.[1] Organic solvents and all other reagents were commercially available and used without further purification. NMR spectra were recorded on a Varian Gemini-300 and a JEOL JNM-AL-400 spectrometers. ^1H NMR chemical shifts in $CDCl_3$ or acetone-d_6 are quoted with respect to TMS and the deuterated solvent signal, respectively, and $^{13}C\{^1H\}$ NMR chemical shifts are quoted with respect to the deuterated solvent signal. Infrared spectra in KBr pellets were obtained on JASCO FT-IR-4100 spectrometers. Fast atom bombardment mass spectra (FAB-MS) and electrospray ionization mass spectra (ESI-MS) were recorded on a JEOL JMS-700N spectrometer and a Waters ACQUITY SQD spectrometer, respectively. Elemental analyses (C, H, N) were performed on a Perkin Elmer 2400II elemental analyzer. Cyclic voltammetry was recorded at room temperature with a BAS ALS-600C electrochemical analyzer by use of a glassy carbon working electrode, a platinum-wire counter electrode, and a Ag/AgCl reference electrode. Cyclic voltammograms at a scan rate of 50 mV/s were recorded for 0.5 mM test solutions of the complex in CH_3CN with 0.1 M $[^nBu_4N][PF_6]$ as a supporting electrolyte. Microwave instrument were performed with EYELA MWO-1000S. The light source used was a high-pressure mercury lamp (Ushio UM102, 100 W). Gas chromatographic analyses were run on a Shimadzu GC-2014AT instrument equipped with a thermal conductivity detector and a Porapak-Q column (1m x 3mm$^{\phi}$).

Preparation of $[(TpRu)_2(\mu\text{-}O)(\mu\text{-}pz)_2]$ (3): a) from $[(TpRu)_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)]$ (1); $[(TpRu)_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)]$ (**1**) (50 mg, 0.066 mmol) and pyrazole (89 mg, 1.31 mmol) were charged into a Teflon-lined autoclave for microwave. Furthermore, EtOH (25 mL) and LiOH (7.8 mg, 0.33 mmol) were added into the autoclave. Then the autoclave was sealed and microwave-heated at 80°C for 4.5h under magnetic stirring. After evaporation, the residue was separated on column chromatography with a silica gel by use of a CH_2Cl_2-acetone (50/1) eluent to give $[(TpRu)_2(\mu\text{-}O_2CMe)(\mu\text{-}O)(\mu\text{-}pz)]$ (**2**) as a blue solid (10.4 mg, 26%) and a CH_2Cl_2-acetone (25/1) eluent to give $[(TpRu)_2(\mu\text{-}O)(\mu\text{-}pz)_2]$ (**3**) as a blue solid (20.6 mg, 41%). **b) from $[(TpRu)_2(\mu\text{-}O_2CMe)(\mu\text{-}O)(\mu\text{-}pz)]$ (2);** $[(TpRu)_2(\mu\text{-}O_2CMe)(\mu\text{-}O)(\mu\text{-}pz)]$ (**2**) (20 mg, 0.026 mmol), pyrazole (35.3 mg, 0.52 mmol), EtOH (25 mL), and LiOH (3.1 mg, 0.13 mmol) were charged into a Teflon-lined autoclave for microwave. Then the autoclave was sealed and microwave-heated at 80°C for 6.5h under magnetic stirring. After evaporation, the residue was separated on column chromatography with a silica gel by use of a CH_2Cl_2-acetone (25/1) eluent to give $[(TpRu)_2(\mu\text{-}O)(\mu\text{-}pz)_2]$ (**3**) (11.3 mg, 56%).

2: IR (KBr, pellet): ν(BH) 2481 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.96 (d, J = 2.2 Hz, 2H, pz), 8.24 (d, J = 1.8 Hz, 2H, pz), 7.86 (d, J = 2.3 Hz, 2H, pz), 7.80 (d, J = 2.3 Hz, 2H, pz), 6.97 (t, J = 2.1 Hz, 2H, pz), 6.27 (d, J = 2.0 Hz, 2H, pz), 6.15 (t, J = 2.1 Hz, 4H, pz), 6.06 (d, J = 1.7 Hz, 2H, pz), 5.86 (t, J = 2.2 Hz, 2H, pz), 5.49 (t, J = 2.0 Hz, 1H, pz), 4.58 (d, J = 1.8 Hz, 2H, pz), 2.00 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 187.1 (s, $O_2\mathit{C}Me$), 146.2 (s, pz), 142.2 (s, pz), 141.7 (s, pz), 140.6 (s, pz), 139.8 (s, pz), 136.0 (s, pz), 135.3 (s, pz), 109.1 (s, pz), 105.9 (s, pz × 3), 23.4 (s,Me). FAB-MS (m/z): 771.1 ($[M]^+$).

3: IR (KBr, pellet): ν(BH) 2480 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.12 (d, J = 2.0 Hz, 2H, pz), 7.91 (d, J = 1.5 Hz, 2H, pz), 7.79 (d, J = 2.0 Hz, 4H, pz), 6.94 (t, J = 2.0 Hz, 2H, pz), 6.10 (d, J = 1.9 Hz, 4H, pz), 5.93 (t, J = 2.0 Hz, 4H, pz), 5.15 (t, J = 1.8 Hz, 2H, pz), 4.91 (d, J = 1.3 Hz, 4H, pz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.8 (s, pz), 141.1 (s, pz), 140.7 (s, pz), 137.5 (s, pz), 135.3 (s, pz), 109.1 (s, pz), 106.7 (s, pz), 104.9 (s, pz). FAB-MS (m/z): 780.1 ($[M+1]^+$). Elemental analysis (%) calcd. for $C_{25}H_{28}N_{16}B_2Cl_2ORu_2$: C 34.78, H 3.27, N 25.96; found: C 34.92, H 2.80, N 25.86.

Preparation of $[(TpRu)_2(\mu\text{-}OH)(\mu\text{-}pz)_2]BF_4$ (4): A diethyl ether (25 mL) solution of $[(TpRu)_2(\mu\text{-}O)(\mu\text{-}pz)_2]$ (**3**) (31 mg, 0.040 mmol) was treated with $HBF_4{\cdot}Et_2O$ (6.0 µL, 0.044 mmol) at room temperature. After stirring for 2h, the resulting precipitate was filtered and washed with diethyl ether to give [(TpRu)$_2$(μ-OH)(μ-pz)$_2$]BF$_4$ (**4**) as a brown powder (31.5 mg, 91%).

4: IR (KBr, pellet): ν(BH) 2513 (w); ν(BF) 1123–1050 (s) cm^{-1}. FAB-MS (*m*/*z*): 780.2 ([M]$^+$).

Preparation of [{TpRu(NO)}$_2$(μ-pz)$_2$](BF$_4$)$_2$ (5): In a Schlenk flask, a distilled acetone (20 mL) solution of [(TpRu)$_2$(μ-O)(μ-pz)$_2$] (**3**) (19.8 mg, 0.026 mmol) was treated with HBF$_4$·Et$_2$O (10.5 μL, 0.077 mmol), and the mixture was stirred at room temperature overnight. After freeze-pump-thaw cycling for three times, NO gas was introduced into the Schlenk flask through a column containing KOH pellets and through an acetone/liquid N$_2$ (-78 ºC) cooled trap to remove impurities. The mixture was exposed to NO gas overnight and evaporated to dryness. The resulting red-brown residue was crystallized from acetone/ether to afford [{TpRu(NO)}$_2$(μ-pz)$_2$](BF$_4$)$_2$ (**5**) as red-brown crystals (23.0 mg, 91%). Complex **5** was also prepared using complex **4** and 2 equiv. of HBF$_4$·Et$_2$O under the similar conditions.

5: IR (KBr, pellet): ν(BH) 2537 (w); ν(N≡O) 1918 (s); ν(BF) 1123–1056 (s) cm^{-1}. ^{1}H NMR (acetone-d$_6$): δ 8.39 (d, *J* = 2.4 Hz, 4H, pz), 8.32 (d, *J* = 2.3 Hz, 2H, pz), 8.26 (d, *J* = 2.1 Hz, 4H, pz), 6.95 (d, *J* = 2.5 Hz, 4H, pz), 6.87 (d, *J* = 2.3 Hz, 2H, pz), 6.73(t, *J* = 2.3 Hz, 4H, pz), 6.39 (t, *J* = 2.2 Hz, 4H, pz × 2). ^{13}C{^{1}H} NMR (acetone-d$_6$): δ 146.5 (s, pz), 145.7 (t, pz), 144.7 (s, pz), 139.7 (t, pz), 138.7 (t, pz), 109.9 (s, pz), 109.4 (s, pz), 108.5 (s, pz). FAB-MS (*m*/*z*): 910.2 ([M+(BF$_4$)]$^+$), 823.2 ([M]$^+$), 793.2 ([M–(NO)]$^+$). Elemental analysis (%) calcd. for $C_{24}H_{26}N_{18}B_4F_8O_2Ru_2$: C 28.94, H 2.63, N 25.31; found: C 29.22, H 2.84, N 25.00.

Preparation of [(TpRu)$_2${μ-N(=O)–N(=O)}(μ-pz)$_2$] (6): [Cp*$_2$Fe] (13 mg, 0.040 mmol) was added to a solution of [{TpRu(NO)}$_2$(μ-pz)$_2$](BF$_4$)$_2$ (**5**) (20 mg, 0.020 mmol) in acetone (20 mL), and the mixture was stirred for 2h at room temperature. After evaporation, the column chromatographic purification with a silica gel afforded [(TpRu)$_2${μ-N(=O)–N(=O)}(μ-pz)$_2$] (**6**) (14.3 mg, 87%) by use of a CH$_2$Cl$_2$ eluent.

6: IR (KBr, pellet): ν(BH) 2490 (w); ν(NO) 1589 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.92 (d, *J* = 2.1 Hz, 2H, pz), 7.83 (d, *J* = 2.3 Hz, 4H, pz), 7.12 (d, *J* = 1.9 Hz, 2H, pz), 6.65 (d, *J* = 1.8 Hz, 4H, pz), 6.31 (t, *J* = 2.1 Hz, 2H, pz), 6.18(t, *J* = 2.2 Hz, 4H, pz), 6.11(d, *J* = 2.1 Hz, 4H, pz), 5.86 (t, *J* = 2.1 Hz, 2H, pz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 143.7 (s, pz), 142.6 (s, pz), 141.4 (s, pz), 135.3 (s, pz), 135.3 (s, pz), 105.9 (s, pz × 2), 105.0 (s, pz). FAB-MS (*m*/*z*): 823.1 ([M]$^+$), 793.1 ([M–(NO)]$^+$), 756.1 ([M–(pz)]$^+$), 726.1 ([M–(NO)–(pz)]$^+$). Elemental analysis (%) calcd. for $C_{24}H_{26}N_{18}B_2O_2Ru_2\cdot(C_3H_6O)_{0.5}$: C 35.97, H 3.43, N 29.61; found: C 36.10, H 3.19, N 29.55.

Reactions of [(TpRu)$_2${μ-N(=O)-N(=O)}(μ-pz)$_2$] (6) with protic acids: To a distilled CH_2Cl_2 (5.0 mL) solution of [(TpRu)$_2${μ-N(=O)-N(=O)}(μ-pz)$_2$] (**6**) (10.6 mg, 0.013 mmol) was added $HBF_4{\cdot}OEt_2$ (2.2 μl, 0.016 mmol). After stirring for 3h at room temperature, additional $HBF_4{\cdot}OEt_2$ (2.2 μl, 0.016 mmol) was added to the reaction mixture. The reaction mixture was stirred for 24h and evaporated to dryness. The residue was crystallized from acetone/ether to afford [{TpRu(NO)}$_2$(μ-pz)$_2$](BF$_4$)$_2$ (**5**) as red-brown crystals (11.7 mg, 90%). The dinitrosyl complex was also obtained using complex **4** and HOTf under the similar conditions.

Conversion of [(TpRu)$_2${μ-N(=O)-N(=O)}(μ-pz)$_2$] (6) to [(TpRu)$_2$(μ-O)(μ-pz)$_2$] (3) or [(TpRu)$_2$(μ-OH)(μ-pz)$_2$]BF$_4$ (4): In the reaction vessel with short optical path length (*ca.* 1 cm), [(TpRu)$_2${μ-N(=O)-N(=O)}(μ-pz)$_2$] (**6**) (12.6 mg, 0.0153 mmol) was dissolved in diethylether (25 mL). The vessel was irradiated with a high-pressure mercury lamp for 2h. After filtration, the filtrate was evaporated, and the residue was crystallized from CH_2Cl_2/hexane to afford [(TpRu)$_2$(μ-O)(μ-pz)$_2$] (**3**) as blue crystals (4.2 mg, 35%). In the presence of $HBF_4{\cdot}Et_2O$ (3.4 μL, 0.025 mmol), the same photochemical reaction was carried out using **6** (20.0 mg, 0.024 mmol). After irradiation for 2h, a brown precipitate appeared. The precipitate was crystallized from CH_2Cl_2/hexane to afford [(TpRu)$_2$(μ-OH)(μ-pz)$_2$]BF$_4$ (**4**) as brown crystals (14.1 mg, 68%). In this reaction, the evolution of N_2O was detected by gas chromatography.

Photo-induced conversion of [(TpRu)$_2$(μ-Cl){μ-N(=O)-N(=O)}(μ-pz)] to [(TpRu)$_2$(μ-Cl)(μ-OH)(μ-pz)]BF$_4$: Irradiation of a diethylether (300 mL) solution of [(TpRu)$_2$(μ-Cl){μ-N(=O)-N(=O)}(μ-pz)] (50 mg, 0.063 mmol) for 1h using a high-pressure mercury lamp gave a blue solution. A brown powder precipitated on addition of $HBF_4{\cdot}Et_2O$ (9.0 μL, 0.064 mmol) to the blue solution. After stirring for 1h, the mixture was filtered. When the color of the filtrate remained, additional irradiation of the filtrate was carried out. The precipitate was crystallized from acetone/ether to afford [(TpRu)$_2$(μ-Cl)(μ-OH)(μ-pz)]BF$_4$ (40.1 mg, 76%).

X-ray Crystal Structure Determinations. Crystallographic data are summarized in Table S1. X-ray quality single crystals were obtained from ether (for **2**·$(ether)_{0.5}$·$(OH_2)_{0.5}$), CH_2Cl_2/hexane (for **3**·CH_2Cl_2), acetone/ether (for **4'**·ether), (acetone + CH_3CN)/ether (for **5**), and benzene/hexane (for **6**·$(C_6H_6)_{1.5}$) respectively. Diffraction data were collected at -180 °C under a stream of cold dinitrogen gas on a Rigaku AFC10 diffractometer equipped with a Rigaku Saturn CCD area detector (**3**·CH_2Cl_2, **5**, and **6**·$(C_6H_6)_{1.5}$) or at room temperature on a Rigaku AFC7 diffractometer equipped with a Rigaku Mercury CCD area detector (**2**·$(ether)_{0.5}$·$(OH_2)_{0.5}$ and **4'**·ether) by using graphite-monochromated Mo Kα radiation. The intensity images were obtained at the exposure of 53.3 s/° (**2**·$(ether)_{0.5}$·$(OH_2)_{0.5}$ and **4'**·ether), 8 s/° (**3**·CH_2Cl_2), 16 s/° (**5**), 2 s/° (**6**·$(C_6H_6)_{1.5}$). The frame data were integrated using a Rigaku CrystalClear program package, and the data sets were corrected for absorption using a REQAB program.

The calculations were performed with a CrystalStructure software package. The structures were solved by direct methods, and refined on F^2 by the full-matrix least squares methods. For **2**·$(ether)_{0.5}$·$(OH_2)_{0.5}$, the asymmetric unit contains two crystallographically independent molecules of **2**·$(ether)_{0.5}$·$(OH_2)_{0.5}$. One of them contains a disorder between μ-O_2CMe group and μ-pz group. For **4'**·ether, the ether crystallization solvent was disordered over two positions with occupancy factors of 0.5/0.5. For **5** and **6**·$(C_6H_6)_{1.5}$, owing to serious disorder problems of the crystallization solvent, we were not able to well define them. Therefore, a SQUEEZE/PLATON technique was applied. Anisotropic refinement was applied to all non-hydrogen atoms, except for the disordered carbon atoms of **2**·$(ether)_{0.5}$·$(OH_2)_{0.5}$ and the crystallization solvents of **2**·$(ether)_{0.5}$·$(OH_2)_{0.5}$ and **4'**·ether. Hydrogen atoms for all structures were put at calculated positions, while the crystallization solvents of **2**·$(ether)_{0.5}$·$(OH_2)_{0.5}$ and **4'**·ether were not included in the calculations.

Table S1. Crystallographic data for [(TpRu)$_2$(μ-O$_2$CMe)(μ-O)(μ-pz)] (**2**), [(TpRu)$_2$(μ-O)(μ-pz)$_2$] (**3**), [(TpRu)$_2$(μ-OH)(μ-pz)$_2$]PF$_6$ (**4'**), [{TpRu(NO)}$_2$(μ-pz)$_2$](BF$_4$)$_2$ (**5**), and [(TpRu)$_2${μ-N(=O)–N(=O)}(μ-pz)$_2$] (**6**)

	2·(ether)$_{0.5}$·(OH$_2$)$_{0.5}$	**3**·CH$_2$Cl$_2$	**4'**·ether	**5**^{e}
formula	$C_{25}H_{32}B_2N_{14}O_4Ru_2$	$C_{25}H_{28}B_2Cl_2N_{16}ORu_2$	$C_{28}H_{37}B_2F_6N_{16}O_2PRu_2$	$C_{24}H_{26}B_4F_8N_{18}O_2Ru_2$
fw	816.38	863.27	998.43	995.96
cryst system	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	*Pnma* (No. 62)	*Cc* (No. 9)	*Pmmn* (No. 59)	*Pnma* (No. 62)
color of crystal	dark blue	blue	red	red
crystal size (mm)	0.60 x 0.20 x 0.10	0.21 x 0.12 x 0.10	0.20 x 0.15 x 0.10	0.20 x 0.04 x 0.04
temperature (K)	296	93	296	93
a (Å)	32.9353(19)	18.521(3)	11.8607(8)	16.337(3)
b (Å)	16.1293(11)	13.621(2)	15.0217(9)	17.461(3)
c (Å)	12.7402(8)	14.615(3)	10.8179(7)	14.116(3)
α (deg)	90	90	90	90
β (deg)	90	117.355(2)	90	90
γ (deg)	90	90	90	90
V (Å^3)	6767.9(7)	3274.8(10)	1927.4(2)	4026.8(12)
Z	8	4	2	4
ρ_{calc} (g cm^{-3})	1.602	1.751	1.720	1.643
μ (cm^{-1})	9.466	11.362	9.068	8.375
$2\theta_{\text{max}}$ (deg)	55.0	55.0	55.0	55.0
no. of all reflns collected	46569	13322	13785	32405
no. of unique reflns	7998	7106	2382	4750
R_{int}	0.0551	0.0229	0.0445	0.0784
no. of obsd reflns ^{a}	7790	6607	2221	3956
no. of parameters	462	433	149	274
R_1 ^{a,b}	0.1053	0.0203	0.0666	0.0705
wR_2 (all data)^c	0.1627	0.0442	0.1315	0.1680
GOF (all data)^d	1.419	0.984	1.299	1.126
CCDC numbers	1832738	1832739	1832740	1832741

^{a} $I > 2\sigma(I)$. ^{b} $R_1 = \Sigma\, ||Fo| - |Fc|| / \Sigma\, |Fo|$. ^{c} w$R_2 = \{\Sigma w\,(Fo^2 - Fc^2)^2 / \Sigma w(Fo^2)^2\}^{1/2}$.

^{d} GOF = $[\{\Sigma w(Fo^2 - Fc^2)^2\}/(No - Np)]^{1/2}$, where No and Np denote the number of data and parameters.

^{e} A CH$_3$CN crystallization solvent may be included, but because of serious disorder problems the SQUEEZE subroutine of the PLATON program suite was used.

Table S1. (Continued)

	6·$(C_6H_6)_{1.5}$
formula	$C_{33}H_{35}B_2N_{18}O_2Ru_2$
fw	939.52
cryst system	monoclinic
space group	$P2_1/c$ (No. 14)
color of crystal	brown
crystal size (mm)	0.27 x 0.21 x 0.04
temperature (K)	93
a (Å)	14.188(6)
b (Å)	13.607(6)
c (Å)	24.098(11)
α (deg)	90
β (deg)	90.120(8)
γ (deg)	90
V (Å^3)	4652(4)
Z	4
ρ_{calc} (g cm^{-3})	1.341
μ (cm^{-1})	6.978
$2\theta_{max}$ (deg)	55.1
no. of all reflns collected	30596
no. of unique reflns	10334
R_{int}	0.0913
no. of obsd reflns [a]	6845
no. of parameters	514
R_1 [a,b]	0.0757
wR_2 (all data)[c]	0.2076
GOF (all data)[d]	1.049
CCDC numbers	1832742

[a] $I > 2\sigma(I)$. [b] $R_1 = \Sigma ||Fo| - |Fc||/\Sigma |Fo|$. [c] w$R_2 = \{\Sigma w (Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2\}^{1/2}$.

[d] GOF = $[\{\Sigma w(Fo^2 - Fc^2)^2\}/(No - Np)]^{1/2}$, where No and Np denote the number of data and parameters.

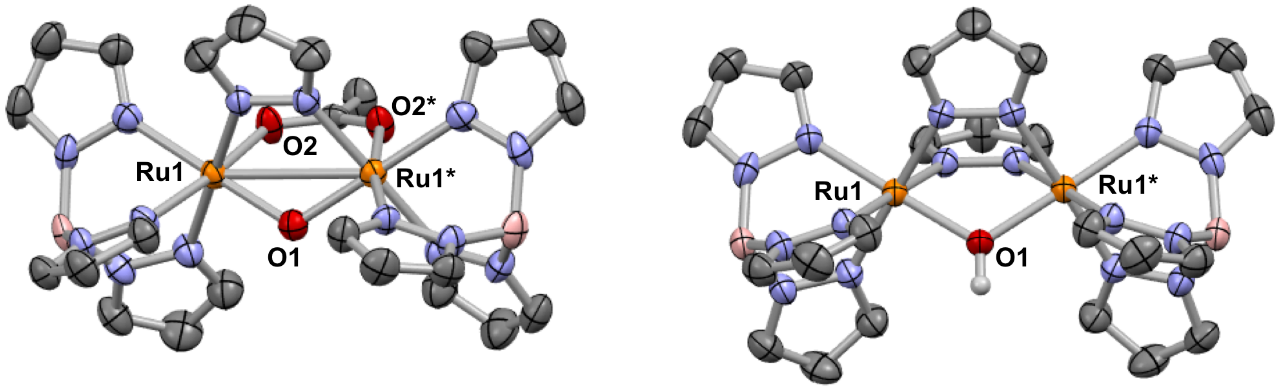

Figure S1. X-ray crystal structures of [(TpRu)$_2$(μ-O$_2$CMe)(μ-O)(μ-pz)] (**2**) (left) and the cation part of [(TpRu)$_2$(μ-OH)(μ-pz)$_2$]PF$_6$ (**4’**) (right). One of the two independent molecules of **2** in the unit cell is shown. Thermal ellipsoids are set at 50% probability level. The counter PF$_6$ ion of **4’**, crystallization solvent, and hydrogen atoms except for hydroxido (OH) proton are omitted for clarity. Selected bond lengths (Å) and angles (°) are as follows. For **2**: Ru1–O1 1.891(3), Ru1–O2 2.086(5); Ru1–O1–Ru1* 117.5(3). For **4’**: Ru1–O1 1.977(4); Ru1–O1–Ru1* 113.5(3).

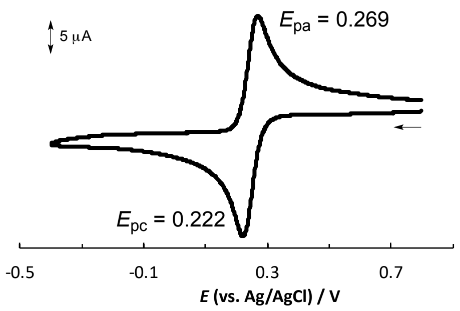

Figure S2. Cyclic voltammogram of [{TpRu(NO)}$_2$(μ-pz)$_2$](BF$_4$)$_2$ (**5**) in CH$_3$CN at room temperature. Conditions: scan rate = 50 mV/s; concentration (sample) = 0.5 mM; concentration ([^{n}Bu$_4$N][PF$_6$]) = 0.1 M; working electrode = glassy carbon; reference electrode = Ag/AgCl; counter electrode = platinum-wire. The open circuit potential was 0.44 V. Ferrocene as a standard ($E_{1/2}$(Fc/Fc$^+$) = +0.45 V vs Ag/AgCl; ΔE = 76 mV).

Reference

1. T. Tanase, N. Takeshita, C. Inoue, M. Kato, S. Yano and K. Sato, *J. Chem. Soc., Dalton Trans.*, 2001, 2293–2302.