Supporting Information

for

Tetranuclear Ruthenium(II) Complex with a Dinucleating Ligand Forming Multi-Mixed-Valence States

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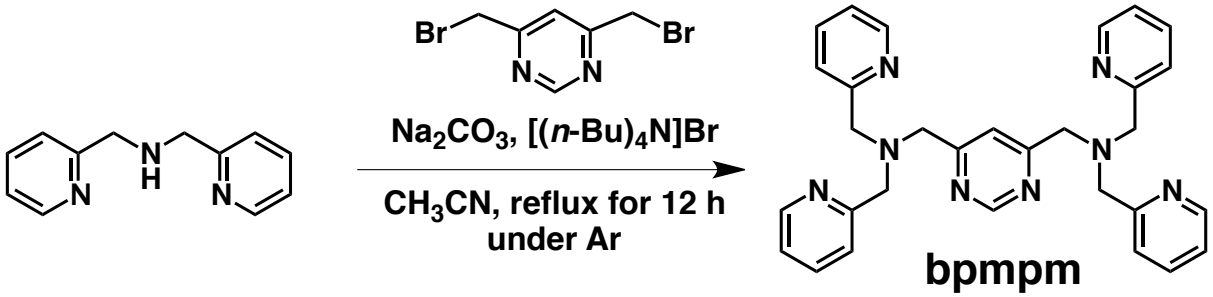
General.

Chemicals and solvents were used as received from Tokyo Chemical Industry (TCI) Co., Wako chemicals, or Sigma-Aldrich Corp. unless otherwise mentioned. 4,6-bis[(*N*,*N*-bis(2'-pyridylmethyl)amino)methyl]pyrimidine (bpmpm) was synthesized with a modified procedure reported in literature (*vide infra*).[1] UV-vis spectra were collected on a Shimadzu UV-3600 spectrophotometer, equipped with a temperature-controller, UNISOK UnispeKs. ^{1}H NMR spectra were recorded on JEOL EX-270 and JNM-ECS 400 spectrometers at room temperature and the chemical shifts of signals were determined with respect to residual proton signals of deuterated solvents. Electrochemical measurements were performed with a BAS CV-1B electrochemical analyzer and an AUTOLAB PGSTAT12 potentiometer in C_3H_7CN in the presence of 0.1 M $[(n\text{-}Bu)_4N]PF_6$ as an electrolyte at 193 K. ESR spectra were collected on a Bruker EMXPlus9.5/2.7 Electron Spin Resonance spectrometer.

Synthesis of 4,6-bis[(*N*,*N*-bis(2'-pyridylmethyl)amino)methyl]pyrimidine (bpmpm). *N*,*N*-bis(2-pyridylmethyl)amine (0.94 g, 4.7 mmol)[2] and 4,6-bis(bromomethyl)pyrimidine[1] (0.70 g, 2.6 mmol) and sodium carbonate (2.7 g, 26 mmol) were refluxed in CH_3CN (50 mL) for 12 h. The mixture was filtrated, and then the solvent of the filtrate was evaporated. The obtained oil was purified by column chromatography on Alumina eluted with a CH_2Cl_2/MeOH (9 : 1 (v/v)) mixed solvent, and then the solvent of the collected fraction was evaporated under vacuum. Yield: 0.55 g (42%). ESI-MS (methanol): m/z = 525.3 ($[M + Na]^+$). ^{1}H NMR ($CDCl_3$): δ 3.79 (s, 4H, pyrimidine-CH_2-N), 3.83 (s, 8H, Py-CH_2-N), 7.06 (d, J = 8 Hz, 4H, H3 of Py), 7.48 (t, J = 8 Hz, 4H, H5 of Py), 7.60 (t, J = 8 Hz, 4H, H4 of Py), 8.04 (s, 1H, H5 of pyrimidine), 8.41 (d, J = 6 Hz, 4H, H6 of Py), 8.93 (s, 1H, H2 of pyrimidine).



Synthesis of $[Ru^{II}_4Cl_5(bpmpm)](PF_6)_3$ (1). The ethanol solution (20 mL) containing bpmpm (0.16 g, 0.32 mmol) and $[Ru_2Cl_4(p\text{-cymene})_2]$ (0.21 g, 0.35 mmol) was refluxed under Ar atmosphere for 24 h. After filtering insoluble solid, red-brownish solid emerged by the

addition of excess NH_4PF_6 and the precipitate was filtered and washed with diethyl ether to remove organic impurities. The obtained powder (0.19 g) was purified by column chromatography on activated alumina as a stationary phase eluted with a CH_2Cl_2/MeOH (7 : 3 (v/v)) mixed solvent, and then the solvent of the collected fraction was evaporated under vacuum. The residual solid was recrystallized from MeOH, filtered, washed with diethyl ether and then dried in vacuo. Yield: 33 mg (9%). Anal. Calcd for $C_{60}H_{60}N_{16}Cl_5Ru_4P_3F_{18}$: C, 35.65; H, 2.99; N, 11.09. Found: C, 35.58; H, 3.02; N, 11.14. ESI-MS (methanol): m/z = 866.8 ($[M - 2PF_6]^{2+}$). ^{1}H NMR (CD_3CN): δ 4.03 (dd, J = 8, 4 Hz, 2H, Ru_2-N-CH_2-pyrimidine), 4.14 (dd, J = 8, 4 Hz, 2H, Ru_1-N-CH_2-pyrimidine), 4.17 and 4.60 (ABq, J_{AB} = 18, 4 Hz, 2H, N-CH_2-Py_3), 4.37 and 4.72 (ABq, J_{AB} = 15, 4 Hz, 2H, N-CH_2-Py_4), 4.44 and 4.91 (ABq, J_{AB} = 18, 4 Hz, 2H, N-CH_2-Py_2), 4.95 and 5.47 (ABq, J_{AB} = 18, 4 Hz, 2H, N-CH_2-Py_1), 6.60 (d, J = 6 Hz, 1H, H3 of Py_3), 6.70 (d, J = 7 Hz, 1H, H3 of Py_4), 6.81 (t, J = 8 Hz, 1H, H4 of Py_3), 6.90-6.92 (m, 2H, H5 of Py_3 and H4 of Py_4), 7.11 (t, J = 8 Hz, 1H, H5 of Py_4), 7.21-7.25 (m, 2H, H5 of Py_1 and H5 of Py_2), 7.33 (s, 1H, H5 of pyrimidine), 7.46 (d, J = 6 Hz, 1H, H3 of Py_2), 7.60 (d, J = 6 Hz, 1H, H3 of Py_1), 7.68-7.70 (m, 2H, H4 of Py_1 and H4 of Py_2), 8.27 (d, J = 6 Hz, 1H, H6 of Py_3), 8.67 (d, J = 6 Hz, 1H, H6 of Py_4), 9.05 (d, J = 6 Hz, 1H, H6 of Py_2), 9.32 (d, J = 6 Hz, 1H, H6 of Py_1), 9.60 (s, 1H, H2 of pyrimidine). UV-Vis (CH_3CN): λ_{max} [nm] = 406.

X-ray Crystallography on $[Ru^{II}_4Cl_5(bpmpm)](PF_6)_3$.

A single crystal of $[Ru^{II}_4Cl_5(bpmpm)](PF_6)_3$ (**1**) was obtained through recrystallization by the vapor diffusion of hexane into the acetone solution of **1**. Diffraction data were collected on a Bruker APEXII diffractometer at 120 K. The structure was solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically and the refinement was carried out with full-matrix least-squares on F. All calculations were performed using the Yadokari-XG crystallographic software package.[3] Crystallographic data for **1**: $C_{60}H_{60}Cl_5N_{16}Ru_4{\cdot}3PF_6$, FW = 2021.87, red, monoclinic, space group $C2/c$, cell parameters: a = 17.580(15) Å, b = 32.562(3) Å, c = 15.875(13) Å, β = 117.5870 (10)°, V = 8054.3 Å^3, T = 120 K, Z = 4, D_{calcd} = 1.667 g cm^{-3}, R_1 = 0.0307 ($I > 2\sigma(I)$) and wR_2 = 0.0787 (all the reflections), GOF = 1.091.

Oxidation and Reduction of Complex 1.

The oxidation of complex **1** (0.1 mM) to generate mixed-valent states were performed using tris(4-bromophenyl)ammouniumyl hexachloroantimonate (TBAH; E = +1.07 vs SCE[4]) as a chemical oxidant in n-C_3H_7CN at 193 K. The reaction profiles were monitored by the rise

of the absorption at 1328 nm assigned to the IVCT band indicating a mixed-valence state formed by addition of 3 equiv of the oxidant. The spectrum of the IVCT band disappeared by addition of 1 equiv of decamethylferrocene (DMFc) as a reductant.

DFT Calculations

We used the hybrid B3LYP DFT method[5,6] implemented with the Gaussian 09 program.[7] The Hay–Wadt basis set (LANL2DZ)[8] was used for the Ru atom, and the D95 basis set[9] for the H, C, N, and O atoms to obtain optimized geometries. Single point calculations were subsequently performed by using a larger basis set, SDD[10] for the Ru atom and D95** for the other atoms.

References.

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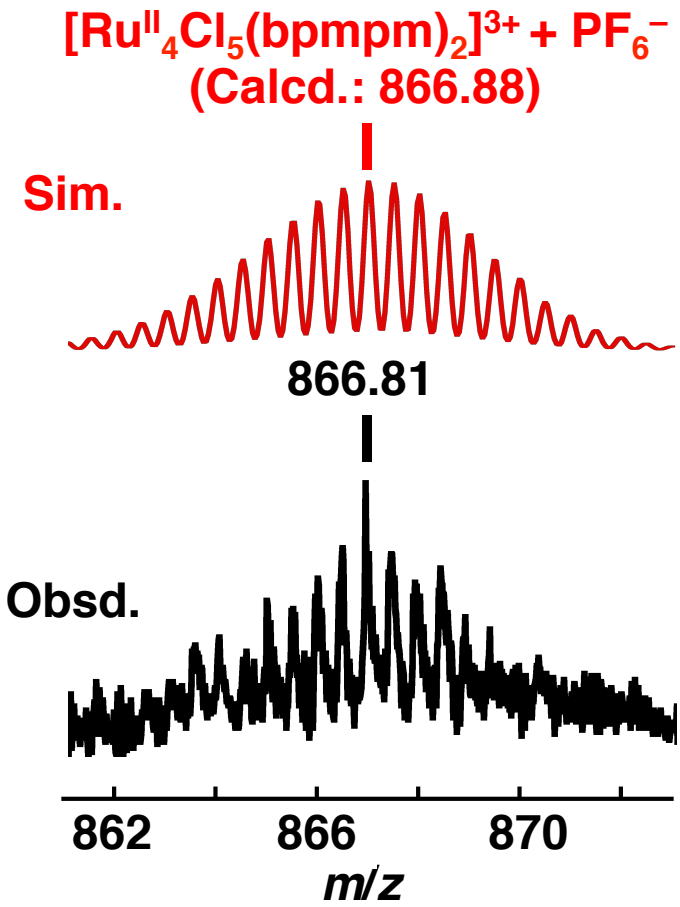

Figure S1. A peak cluster in the ESI-TOF-MS spectrum of **1** (below, black) in methanol and the computer simulation (above, red).

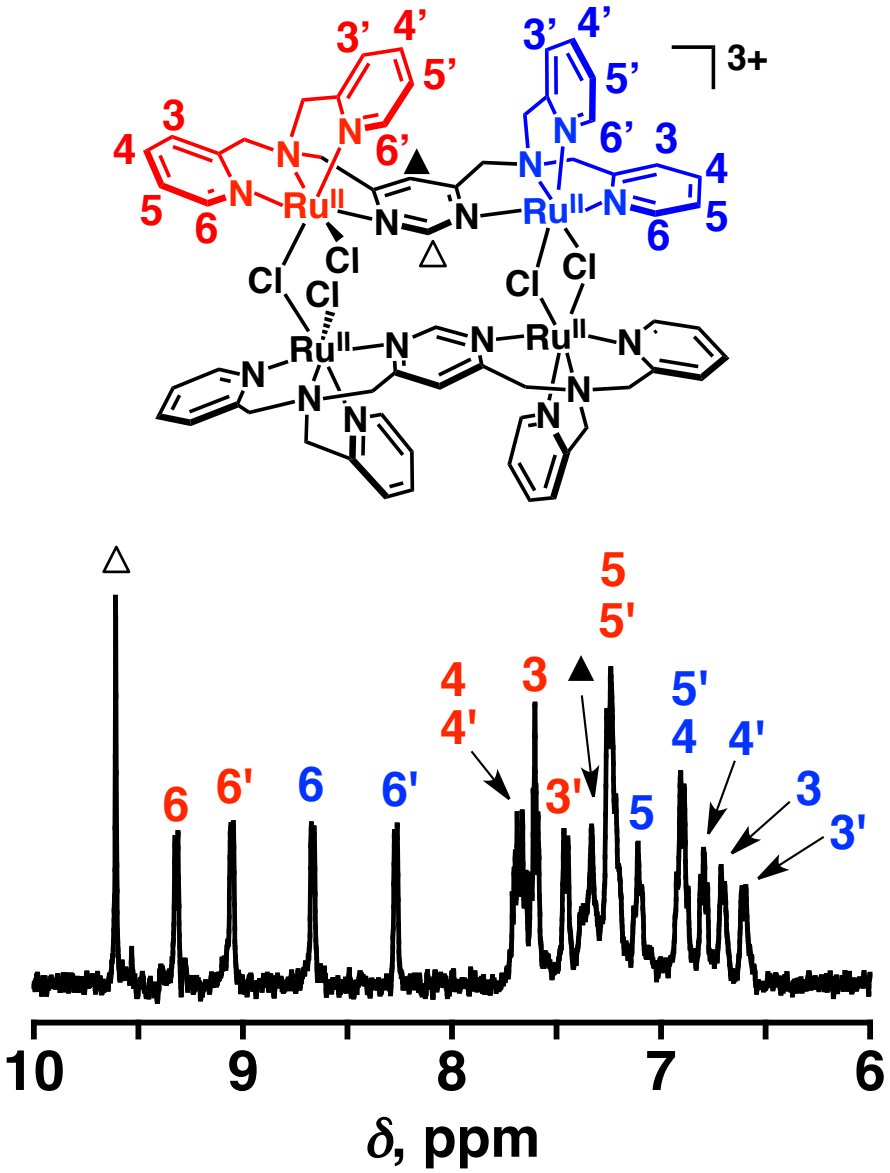

Figure S2. ^{1}H NMR spectrum of **1** in CD_3CN and peak assignments.

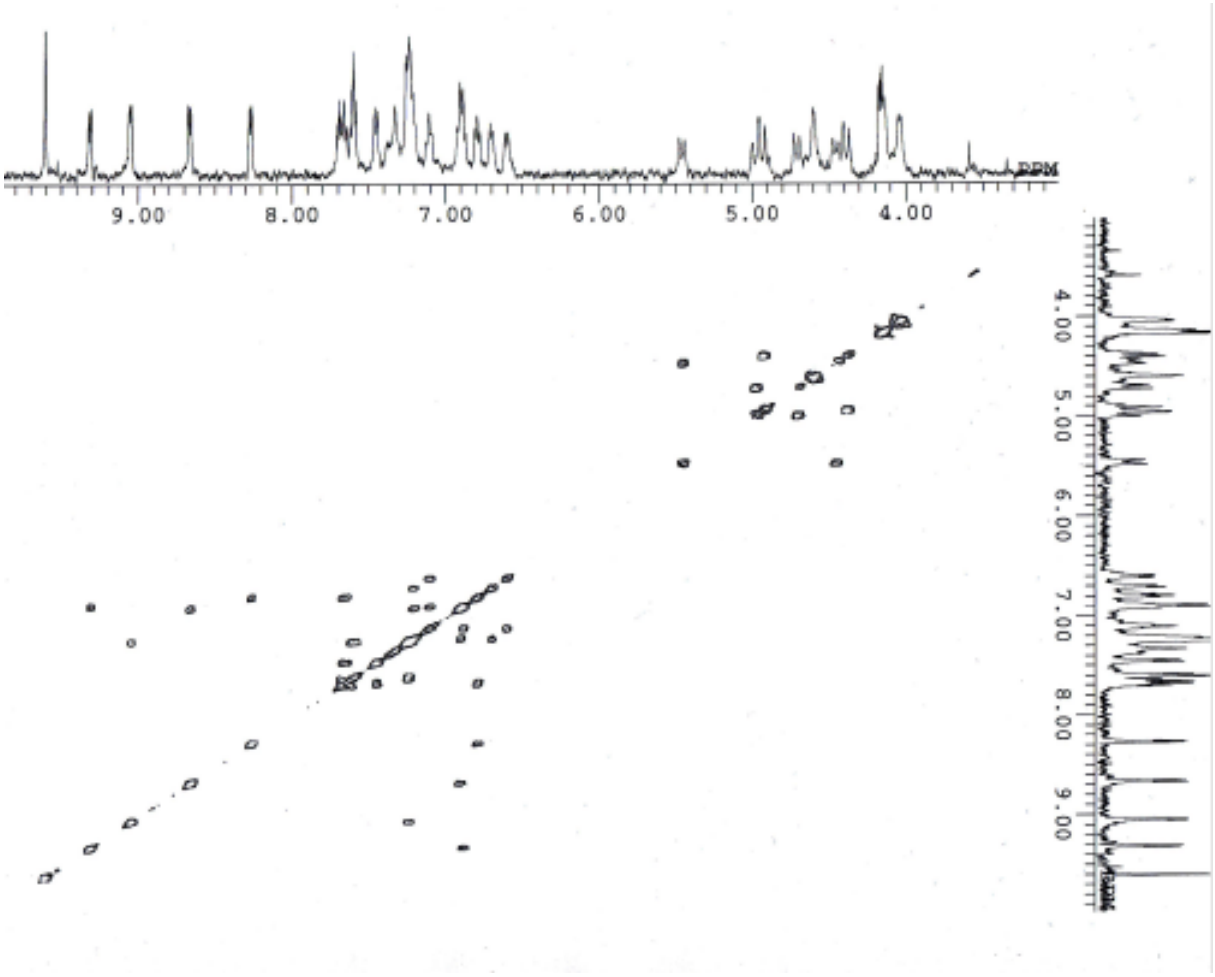

Figure S3. ^{1}H-^{1}H COSY spectrum of **1** in CD_3CN at room temperature.

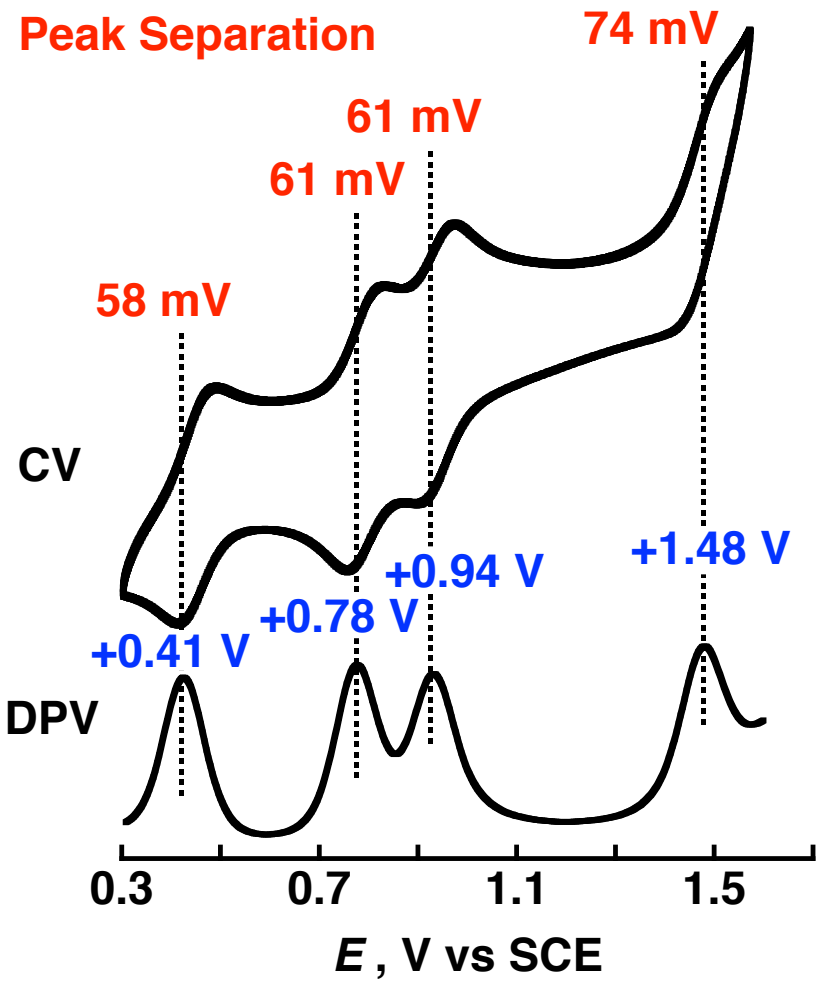

Figure S4. CV (above) and DPV (below) of **1** in n-C_3H_7CN in the presence of [(n-Bu)$_4$N](PF$_6$) (0.1 M) as an electrolyte at 193 K.

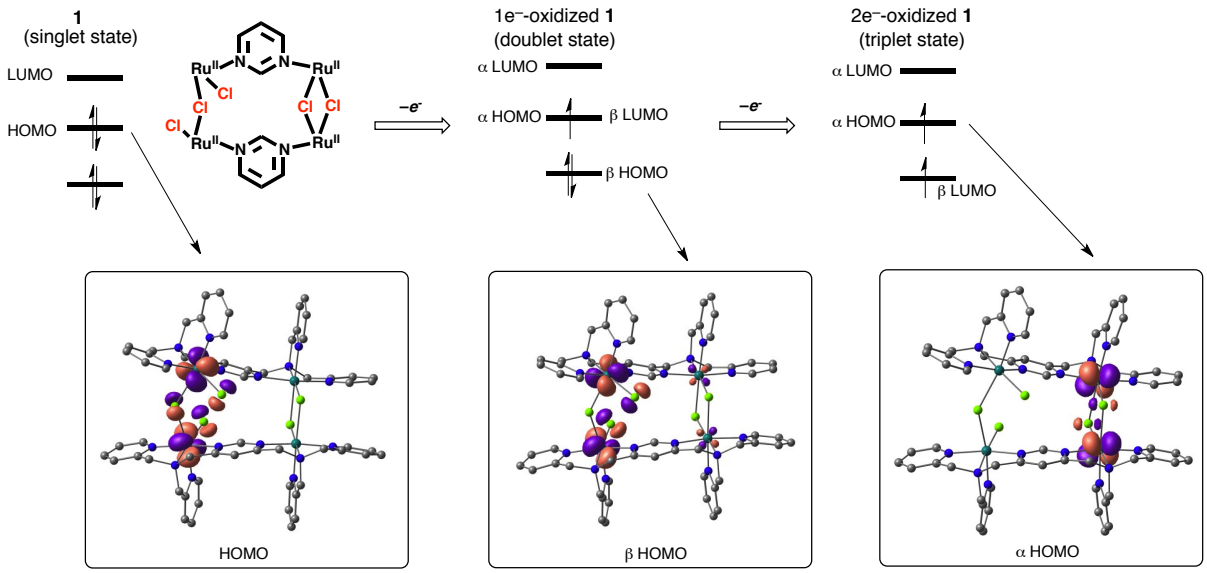

Figure S5. Electronic configurations of **1**, 1e⁻-oxidized **1**, and 2e⁻-oxidized **1** at the B3LYP/SDD level of theory.

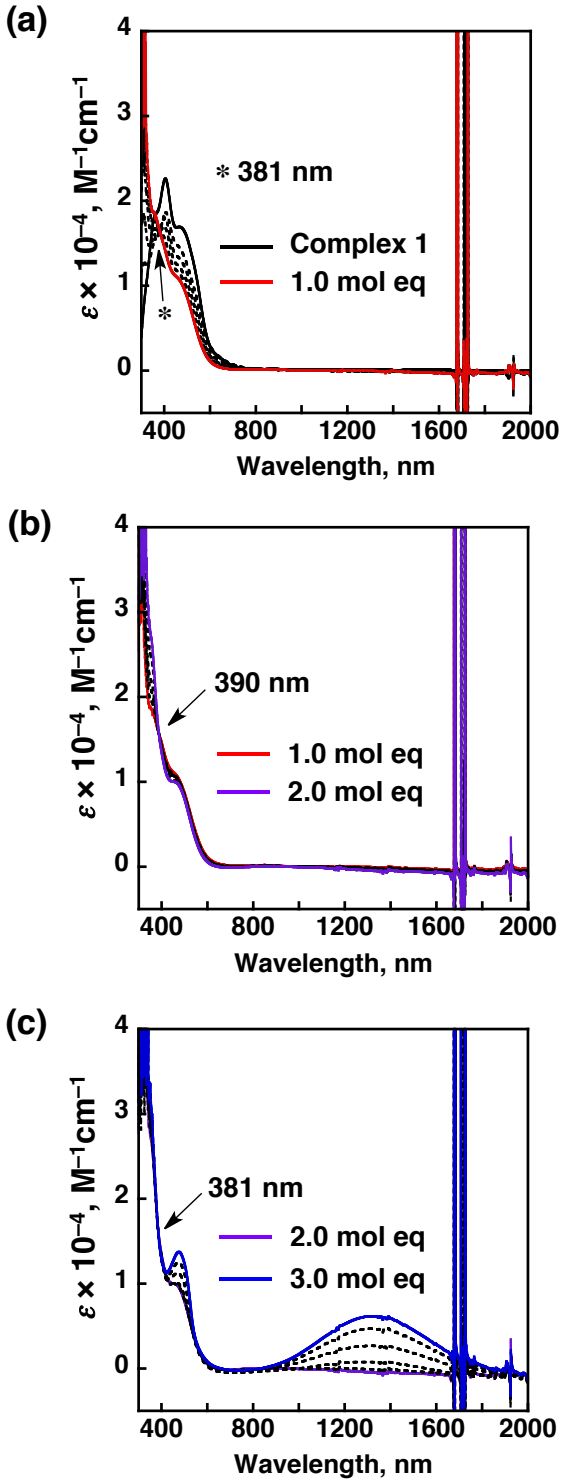

Figure S6. Spectral changes of **1** for every 0.2 eq addition of TBAPH in C_3H_7CN (sample concentration: 0.1 mM) at 193 K. The graphs indicate the changes during the reactions using TBAPH a) 0–1 eq (black to red), b) 1-2 eq and c) 2-3 eq. The spectra of each complex are indicated as the black (complex **1**), red (**1** with 1 mol eq oxidant), purple (**1** with 2 mol eq oxidant) and blue lines (**1** with 3 mol eq oxidant) in the graphs, respectively.

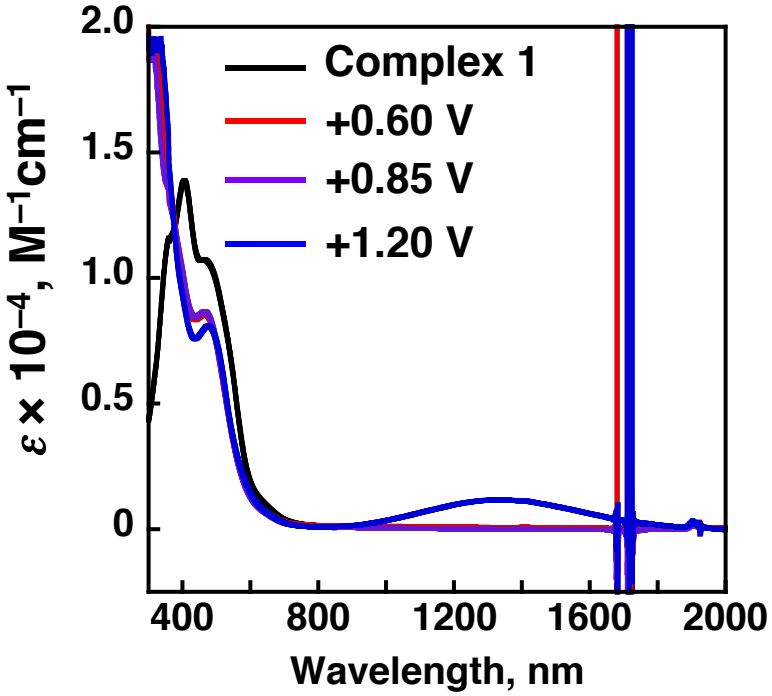

Figure S7. Spectral changes of every 9.65 mC during the electrochemical oxidation of **1** in C_3H_7CN (sample concentration: 0.05 mM, sample volume: 2 mL; $[(n\text{-}Bu)_4N]PF_6$ (0.1 M) as an electrolyte) at 193 K. Black: the initial spectrum, red: the spectrum of **1** after $1e^-$ oxidation with the charged potential of +0.60 V vs SCE, purple: the spectrum of **1** after further $1e^-$ oxidation (total $2e^-$ oxidation) with the charged potential of +0.85 V vs SCE, blue: the spectrum of **1** after further $1e^-$ oxidation (total $3e^-$ oxidation) with the charged potential of +1.20 V vs SCE.

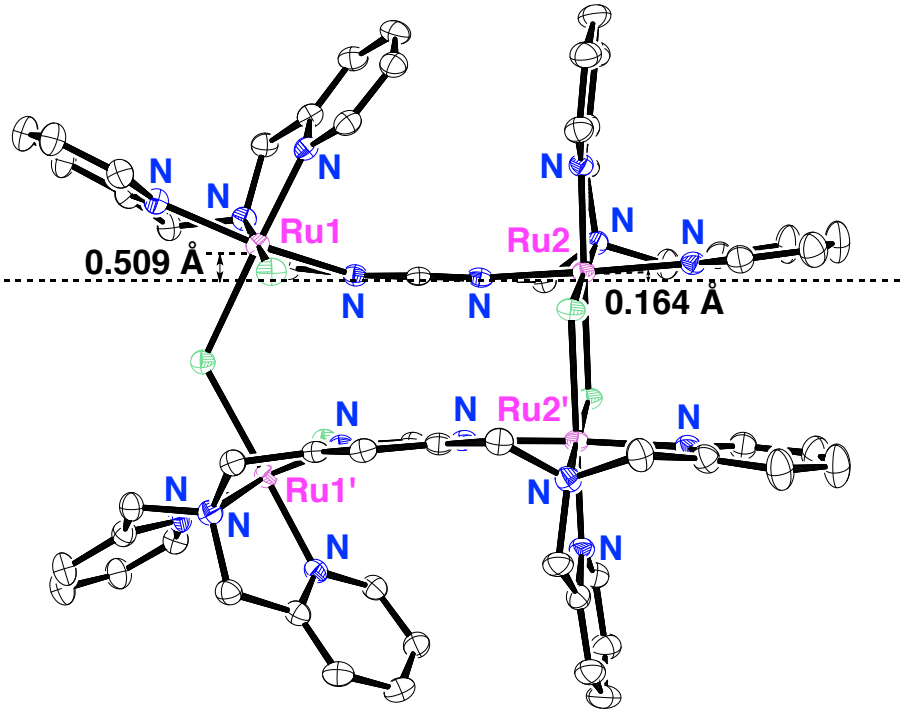

Figure S8. A view of the crystal structure of complex **1** to clarify the distortion.

Table S1. Selected Bond Lengths (Å) and Angles (°) of **1**.

Bond lengths (Å)			
Ru1–Ru2	6.161(6)	Ru1–N5	2.027(2)
Ru1-Cl1	2.436(9)	Ru2–Cl2	2.442(6)
Ru1-Cl3	2.460(5)	Ru2–N2	2.071(2)
Ru1-N1	2.056(2)	Ru2–N6	2.050(3)
Ru1–N3	2.061(3)	Ru2–N7	2.058(2)
Ru1–N4	2.065(2)	Ru2–N8	2.028(2)
Ru1···Ru1’	4.365(5)	Ru2···Ru2’	3.626(4)
Bond Angles (°)			
Cl1-Ru1-Cl3	89.71(3)	Cl2-Ru2-N2	99.86(6)
Cl1-Ru1-N3	176.71(7)	Cl2-Ru2-N6	178.51(7)
Cl1-Ru1-N4	96.50(7)	Cl2-Ru2-N7	95.40(7)
Cl1-Ru1-N5	95.42(7)	Cl2-Ru2-N8	96.87(7)
Cl1-Ru1-N1	100.29(7)	Cl2-Ru2-Cl2’	84.18(2)
Cl3-Ru1-N3	92.19(7)	N2-Ru2-N6	81.62(9)
Cl3-Ru1-N4	88.48(7)	N2-Ru2-N7	164.52(9)
Cl3-Ru1-N5	174.35(7)	N2-Ru2-N8	94.03(9)
Cl3-Ru1-N1	94.90(7)	N6-Ru2-N7	83.1(1)
N3-Ru1-N4	80.9(1)	N6-Ru2-N8	83.16(9)
N3-Ru1-N5	82.80(9)	N7-Ru2-N8	86.7(1)
N1-Ru1-N3	82.24(9)	N6-Ru2-Cl2’	95.77(7)
N4-Ru1-N5	93.29(9)	N7-Ru2-Cl2’	92.60(7)
N1-Ru1-N4	162.9(1)	N8-Ru2-Cl2’	178.77(7)
N1-Ru1-N5	81.86(9)	N7-Ru2-Cl2’	92.60(7)
		N8-Ru2-Cl2’	178.77(7)

Table S2. Cartesian Coordinates of **1** at the B3LYP/LANL2DZ level of theory.

Ru	−3.013088	−1.654640	−1.023488
Ru	2.896581	−2.272052	0.792651
Cl	−3.018269	−0.905617	1.449329
Cl	1.728436	−1.151836	2.746961
Cl	3.892754	0.000004	0.000013
N	3.793746	−3.251613	−0.849511
N	4.751426	−2.609199	1.677349
N	2.409640	−4.182942	1.347864
N	1.321009	−2.116589	−0.533684
N	−0.934958	−1.780108	−1.230813
N	−2.975080	−2.220060	−3.044739
N	−5.074295	−1.681241	−1.375583
N	−3.063653	−3.677125	−0.718996
C	5.283276	−3.004631	−0.693016
H	5.477104	−1.994416	−1.069052
H	5.872261	−3.716831	−1.285482
C	5.690989	−3.045940	0.774429
C	6.974605	−3.421687	1.190843
H	7.702899	−3.772689	0.465702
C	7.309694	−3.333555	2.557093
H	8.299538	−3.621645	2.897855
C	6.343874	−2.872502	3.469732
H	6.564738	−2.790928	4.528775
C	5.069714	−2.523096	2.995346
H	4.280418	−2.163644	3.646672
C	3.449485	−4.732758	−0.815374
H	2.720857	−4.933104	−1.610720
H	4.339778	−5.328836	−1.049058
C	2.855667	−5.172448	0.511081
C	2.733727	−6.527303	0.851716
H	3.111460	−7.292334	0.179217
C	2.131615	−6.881484	2.072813
H	2.040424	−7.924960	2.358503

C	1.665995	-5.858707	2.920561
H	1.204894	-6.086280	3.876004
C	1.822662	-4.521545	2.533422
H	1.504736	-3.687773	3.149581
C	3.187909	-2.574854	-2.065550
H	3.359289	-3.152068	-2.984319
H	3.663223	-1.592954	-2.170047
C	1.707455	-2.328673	-1.837761
C	0.767764	-2.235981	-2.871834
H	1.070705	-2.362780	-3.904985
C	-0.560001	-1.938109	-2.547017
C	0.014989	-1.862440	-0.271221
H	-0.268353	-1.707374	0.761602
C	-1.650939	-1.698011	-3.571153
H	-1.754812	-0.613955	-3.699667
H	-1.398437	-2.140127	-4.543271
C	-4.182949	-1.528755	-3.654549
H	-4.408546	-1.920468	-4.654938
H	-3.934130	-0.465776	-3.742623
C	-5.371924	-1.683761	-2.719205
C	-6.692449	-1.790283	-3.172421
H	-6.904343	-1.795658	-4.237403
C	-7.738353	-1.893942	-2.232741
H	-8.767803	-1.983314	-2.565929
C	-7.424546	-1.894192	-0.862108
H	-8.199456	-1.984504	-0.108101
C	-6.080820	-1.788061	-0.469027
H	-5.784830	-1.785788	0.573661
C	-3.081617	-3.734495	-3.182967
H	-4.005841	-3.973658	-3.721691
H	-2.255073	-4.101237	-3.803487
C	-3.085358	-4.453364	-1.846342
C	-3.139283	-5.853535	-1.768985
H	-3.163377	-6.446527	-2.678959
C	-3.176397	-6.475523	-0.508913

H	−3.229614	−7.556964	−0.430557
C	−3.151262	−5.669671	0.645979
H	−3.183917	−6.106764	1.638282
C	−3.092103	−4.278336	0.507210
H	−3.071566	−3.613699	1.362697
Ru	−3.013091	1.654639	1.023488
Ru	2.896580	2.272052	−0.792645
Cl	−3.018265	0.905617	−1.449329
Cl	1.728444	1.151821	−2.746954
N	3.793735	3.251626	0.849512
N	4.751427	2.609199	−1.677341
N	2.409637	4.182937	−1.347875
N	1.321005	2.116594	0.533686
N	−0.934961	1.780110	1.230814
N	−2.975087	2.220062	3.044739
N	−5.074298	1.681239	1.375583
N	−3.063655	3.677125	0.718995
C	5.283268	3.004655	0.693022
H	5.477099	1.994445	1.069069
H	5.872245	3.716864	1.285485
C	5.690984	3.045954	−0.774422
C	6.974599	3.421704	−1.190836
H	7.702889	3.772715	−0.465696
C	7.309693	3.333560	−2.557084
H	8.299537	3.621650	−2.897845
C	6.343878	2.872492	−3.469721
H	6.564747	2.790905	−4.528763
C	5.069720	2.523083	−2.995336
H	4.280428	2.163617	−3.646660
C	3.449466	4.732770	0.815366
H	2.720830	4.933116	1.610704
H	4.339753	5.328854	1.049054
C	2.855657	5.172449	−0.511096
C	2.733716	6.527302	−0.851742
H	3.111445	7.292339	−0.179246

C	2.131613	6.881474	-2.072846
H	2.040423	7.924947	-2.358545
C	1.666001	5.858690	-2.920590
H	1.204907	6.086255	-3.876038
C	1.822666	4.521531	-2.533440
H	1.504747	3.687753	-3.149596
C	3.187902	2.574868	2.065553
H	3.359277	3.152085	2.984320
H	3.663218	1.592969	2.170056
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H	1.070696	2.362795	3.904987
C	-0.560006	1.938114	2.547018
C	0.014986	1.862440	0.271223
H	-0.268354	1.707368	-0.761600
C	-1.650945	1.698016	3.571154
H	-1.754818	0.613961	3.699670
H	-1.398446	2.140134	4.543272
C	-4.182954	1.528753	3.654549
H	-4.408552	1.920466	4.654938
H	-3.934132	0.465775	3.742624
C	-5.371929	1.683756	2.719204
C	-6.692454	1.790274	3.172420
H	-6.904349	1.795647	4.237401
C	-7.738358	1.893931	2.232739
H	-8.767808	1.983302	2.565926
C	-7.424549	1.894186	0.862107
H	-8.199459	1.984500	0.108099
C	-6.080823	1.788059	0.469026
H	-5.784831	1.785791	-0.573661
C	-3.081628	3.734496	3.182966
H	-4.005857	3.973656	3.721682
H	-2.255090	4.101241	3.803493
C	-3.085361	4.453364	1.846340
C	-3.139283	5.853535	1.768983

H	−3.163379	6.446528	2.678956
C	−3.176396	6.475522	0.508911
H	−3.229615	7.556964	0.430554
C	−3.151264	5.669670	−0.645981
H	−3.183921	6.106762	−1.638285
C	−3.092105	4.278335	−0.507212
H	−3.071574	3.613697	−1.362698

Table S3. Cartesian Coordinates of $1e^-$-oxidized **1** at the B3LYP/LANL2DZ level of theory.

Ru	−3.031029	−1.709932	−0.941004
Ru	2.955291	−2.266417	0.735847
Cl	−2.955578	−0.826693	1.490711
Cl	1.844767	−1.235986	2.683833
Cl	3.875641	−0.000001	−0.000001
N	3.800183	−3.221994	−0.955591
N	4.846803	−2.619873	1.547477
N	2.538020	−4.216636	1.284274
N	1.313859	−2.134362	−0.571881
N	−0.972475	−1.867692	−1.203778
N	−3.058267	−2.370013	−2.932985
N	−5.106210	−1.723269	−1.228041
N	−3.178028	−3.716806	−0.539643
C	5.298556	−2.969593	−0.847220
H	5.480605	−1.957236	−1.223097
H	5.860477	−3.674509	−1.471445
C	5.754832	−3.037378	0.603865
C	7.049444	−3.425401	0.970566
H	7.754336	−3.762294	0.216349
C	7.426859	−3.371940	2.327946
H	8.425538	−3.671700	2.630426
C	6.491311	−2.933252	3.282303
H	6.744691	−2.882431	4.335809
C	5.203950	−2.569227	2.857548
H	4.439246	−2.231573	3.547961
C	3.473989	−4.711659	−0.933617
H	2.697021	−4.901112	−1.684023
H	4.353905	−5.288070	−1.240380
C	2.972805	−5.181913	0.416470
C	2.910264	−6.542813	0.747694
H	3.275651	−7.290146	0.049335
C	2.381335	−6.925894	1.993589
H	2.335775	−7.974164	2.272254

C	1.926815	-5.926603	2.874443
H	1.520949	-6.177433	3.848644
C	2.022849	-4.581753	2.494899
H	1.709254	-3.771996	3.142502
C	3.152537	-2.549507	-2.153417
H	3.313192	-3.124939	-3.073862
H	3.610687	-1.561595	-2.275785
C	1.673057	-2.341597	-1.882471
C	0.698738	-2.294311	-2.889822
H	0.972636	-2.435326	-3.929649
C	-0.629163	-2.037885	-2.530082
C	0.011865	-1.913722	-0.272086
H	-0.253009	-1.754904	0.765031
C	-1.757625	-1.871127	-3.530540
H	-1.875673	-0.797941	-3.723096
H	-1.528122	-2.367200	-4.482094
C	-4.288029	-1.706199	-3.537742
H	-4.543017	-2.147526	-4.509283
H	-4.041848	-0.649305	-3.687537
C	-5.445593	-1.812276	-2.558684
C	-6.778188	-1.957040	-2.963059
H	-7.024685	-2.030343	-4.018002
C	-7.792891	-2.013218	-1.985334
H	-8.830998	-2.133973	-2.279448
C	-7.436446	-1.927432	-0.627770
H	-8.186712	-1.981796	0.153964
C	-6.082344	-1.784908	-0.284767
H	-5.755110	-1.719943	0.746442
C	-3.161086	-3.892014	-2.999254
H	-4.029510	-4.165606	-3.609120
H	-2.280625	-4.286966	-3.520470
C	-3.275603	-4.538263	-1.630231
C	-3.478818	-5.919703	-1.488290
H	-3.567483	-6.550240	-2.368489
C	-3.584497	-6.473617	-0.200283

H	-3.756924	-7.537750	-0.072214
C	-3.476753	-5.622001	0.916733
H	-3.562412	-6.007047	1.927297
C	-3.274456	-4.251998	0.713232
H	-3.198478	-3.551796	1.536707
Ru	-3.031027	1.709933	0.941004
Ru	2.955293	2.266415	-0.735848
Cl	-2.955578	0.826695	-1.490711
Cl	1.844768	1.235986	-2.683834
N	3.800186	3.221991	0.955591
N	4.846805	2.619870	-1.547477
N	2.538023	4.216635	-1.284273
N	1.313861	2.134361	0.571881
N	-0.972473	1.867692	1.203777
N	-3.058264	2.370014	2.932985
N	-5.106208	1.723272	1.228041
N	-3.178025	3.716807	0.539643
C	5.298559	2.969588	0.847220
H	5.480607	1.957231	1.223096
H	5.860480	3.674504	1.471445
C	5.754835	3.037375	-0.603865
C	7.049447	3.425396	-0.970567
H	7.754339	3.762289	-0.216350
C	7.426861	3.371936	-2.327946
H	8.425541	3.671695	-2.630427
C	6.491313	2.933250	-3.282304
H	6.744693	2.882429	-4.335810
C	5.203951	2.569225	-2.857549
H	4.439248	2.231573	-3.547962
C	3.473993	4.711656	0.933618
H	2.697025	4.901109	1.684024
H	4.353909	5.288067	1.240381
C	2.972809	5.181911	-0.416469
C	2.910270	6.542812	-0.747692
H	3.275657	7.290144	-0.049332

C	2.381340	6.925894	-1.993586
H	2.335781	7.974164	-2.272251
C	1.926820	5.926604	-2.874441
H	1.520953	6.177435	-3.848642
C	2.022853	4.581754	-2.494898
H	1.709257	3.771997	-3.142501
C	3.152539	2.549504	2.153416
H	3.313195	3.124934	3.073862
H	3.610689	1.561591	2.275784
C	1.673059	2.341594	1.882471
C	0.698741	2.294309	2.889822
H	0.972639	2.435323	3.929649
C	-0.629160	2.037884	2.530082
C	0.011867	1.913722	0.272086
H	-0.253007	1.754905	-0.765031
C	-1.757623	1.871127	3.530540
H	-1.875672	0.797941	3.723095
H	-1.528120	2.367199	4.482094
C	-4.288027	1.706201	3.537742
H	-4.543015	2.147529	4.509283
H	-4.041846	0.649307	3.687537
C	-5.445591	1.812280	2.558684
C	-6.778186	1.957044	2.963059
H	-7.024683	2.030348	4.018002
C	-7.792889	2.013223	1.985335
H	-8.830995	2.133979	2.279448
C	-7.436445	1.927437	0.627771
H	-8.186710	1.981802	-0.153963
C	-6.082342	1.784912	0.284767
H	-5.755109	1.719946	-0.746441
C	-3.161082	3.892016	2.999254
H	-4.029505	4.165608	3.609121
H	-2.280620	4.286967	3.520470
C	-3.275598	4.538264	1.630232
C	-3.478813	5.919705	1.488291

H	−3.567477	6.550242	2.368489
C	−3.584492	6.473619	0.200283
H	−3.756917	7.537752	0.072215
C	−3.476748	5.622003	−0.916732
H	−3.562407	6.007049	−1.927296
C	−3.274453	4.252000	−0.713232
H	−3.198476	3.551798	−1.536707

Table S4. Cartesian Coordinates of $2e^-$-oxidized **1** at the B3LYP/LANL2DZ level of theory.

Ru	−3.012648	−1.744730	−0.903250
Ru	2.968217	−2.366261	0.713151
Cl	−2.848911	−0.783216	1.498135
Cl	1.892335	−1.358620	2.614499
Cl	3.813637	−0.000003	−0.000004
N	3.790264	−3.298955	−1.016095
N	4.906660	−2.702992	1.424123
N	2.591850	−4.326487	1.257944
N	1.322808	−2.238425	−0.620691
N	−0.975905	−1.962212	−1.207548
N	−3.098198	−2.449374	−2.877949
N	−5.096884	−1.715566	−1.149290
N	−3.252780	−3.738932	−0.452964
C	5.293344	−3.028426	−0.967217
H	5.448832	−2.007942	−1.334117
H	5.829565	−3.718155	−1.628116
C	5.795534	−3.111765	0.459749
C	7.098942	−3.493581	0.797009
H	7.789635	−3.822417	0.026341
C	7.503975	−3.445897	2.146913
H	8.509434	−3.744262	2.428040
C	6.586207	−3.014779	3.122952
H	6.860977	−2.968959	4.171421
C	5.288871	−2.654089	2.730904
H	4.543798	−2.328675	3.447129
C	3.479381	−4.796129	−0.990614
H	2.685252	−4.989881	−1.721527
H	4.357441	−5.359331	−1.324482
C	3.020715	−5.277804	0.369931
C	2.985905	−6.640967	0.693858
H	3.343115	−7.379893	−0.017645
C	2.494023	−7.040559	1.950934
H	2.471049	−8.091608	2.222480

C	2.045688	-6.055338	2.851077
H	1.666146	-6.320303	3.832143
C	2.112487	-4.706587	2.479409
H	1.797705	-3.912619	3.145096
C	3.134037	-2.634984	-2.216923
H	3.301873	-3.219644	-3.129203
H	3.590660	-1.647526	-2.348334
C	1.660460	-2.438734	-1.936101
C	0.666399	-2.392479	-2.925475
H	0.920942	-2.540470	-3.969594
C	-0.656266	-2.139724	-2.543022
C	0.025933	-2.012852	-0.292773
H	-0.228442	-1.853764	0.746625
C	-1.805992	-1.990968	-3.522375
H	-1.912854	-0.923708	-3.752790
H	-1.604392	-2.521940	-4.461270
C	-4.331053	-1.776844	-3.474237
H	-4.610733	-2.237019	-4.429443
H	-4.070830	-0.728103	-3.654764
C	-5.467330	-1.844154	-2.468642
C	-6.808876	-1.997808	-2.838059
H	-7.081286	-2.101902	-3.884013
C	-7.800441	-2.026615	-1.834919
H	-8.844953	-2.157557	-2.100990
C	-7.412187	-1.902672	-0.488802
H	-8.144312	-1.937683	0.311013
C	-6.050717	-1.749353	-0.181680
H	-5.700875	-1.655886	0.839847
C	-3.228980	-3.972902	-2.906884
H	-4.071651	-4.250090	-3.549895
H	-2.332173	-4.396373	-3.375199
C	-3.411869	-4.574910	-1.525565
C	-3.725173	-5.931975	-1.353447
H	-3.863991	-6.574314	-2.218489
C	-3.877746	-6.445624	-0.052929

H	−4.137357	−7.488885	0.098464
C	−3.705750	−5.579927	1.045449
H	−3.827840	−5.934301	2.063499
C	−3.396667	−4.234626	0.811702
H	−3.276831	−3.523679	1.620865
Ru	−3.012644	1.744734	0.903249
Ru	2.968221	2.366258	−0.713154
Cl	−2.848909	0.783220	−1.498136
Cl	1.892336	1.358624	−2.614504
N	3.790271	3.298945	1.016095
N	4.906665	2.702987	−1.424126
N	2.591857	4.326487	−1.257939
N	1.322812	2.238421	0.620689
N	−0.975901	1.962211	1.207547
N	−3.098191	2.449376	2.877949
N	−5.096880	1.715574	1.149290
N	−3.252772	3.738937	0.452964
C	5.293351	3.028411	0.967215
H	5.448836	2.007926	1.334111
H	5.829574	3.718137	1.628116
C	5.795539	3.111754	−0.459750
C	7.098949	3.493568	−0.797010
H	7.789643	3.822400	−0.026341
C	7.503981	3.445888	−2.146914
H	8.509440	3.744252	−2.428041
C	6.586211	3.014777	−3.122954
H	6.860980	2.968960	−4.171423
C	5.288875	2.654088	−2.730907
H	4.543800	2.328678	−3.447133
C	3.479392	4.796120	0.990618
H	2.685264	4.989871	1.721533
H	4.357453	5.359319	1.324487
C	3.020726	5.277800	−0.369925
C	2.985918	6.640964	−0.693847
H	3.343130	7.379887	0.017658

C	2.494034	7.040561	-1.950921
H	2.471062	8.091611	-2.222463
C	2.045696	6.055344	-2.851066
H	1.666153	6.320314	-3.832130
C	2.112493	4.706592	-2.479403
H	1.797707	3.912626	-3.145092
C	3.134044	2.634971	2.216921
H	3.301882	3.219627	3.129202
H	3.590665	1.647512	2.348328
C	1.660466	2.438725	1.936100
C	0.666405	2.392469	2.925473
H	0.920949	2.540458	3.969593
C	-0.656261	2.139720	2.543021
C	0.025937	2.012852	0.292771
H	-0.228439	1.853768	-0.746627
C	-1.805986	1.990966	3.522373
H	-1.912852	0.923705	3.752787
H	-1.604385	2.521935	4.461270
C	-4.331048	1.776849	3.474237
H	-4.610727	2.237023	4.429443
H	-4.070828	0.728107	3.654763
C	-5.467325	1.844162	2.468643
C	-6.808871	1.997819	2.838060
H	-7.081281	2.101912	3.884015
C	-7.800436	2.026628	1.834921
H	-8.844948	2.157571	2.100992
C	-7.412184	1.902685	0.488803
H	-8.144308	1.937696	-0.311011
C	-6.050713	1.749363	0.181681
H	-5.700873	1.655896	-0.839846
C	-3.228969	3.972905	2.906885
H	-4.071639	4.250096	3.549896
H	-2.332161	4.396374	3.375199
C	-3.411858	4.574914	1.525566
C	-3.725159	5.931981	1.353449

H	-3.863974	6.574319	2.218492
C	-3.877731	6.445630	0.052932
H	-4.137340	7.488892	-0.098461
C	-3.705738	5.579934	-1.045447
H	-3.827828	5.934309	-2.063497
C	-3.396658	4.234631	-0.811701
H	-3.276825	3.523685	-1.620864