Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Supporting Information

Exchange of Equatorial Ligands in Protein-bound Paddlewheel Ru_2^{5+} Complexes: New Insights from X-ray Crystallography and Quantum Chemistry

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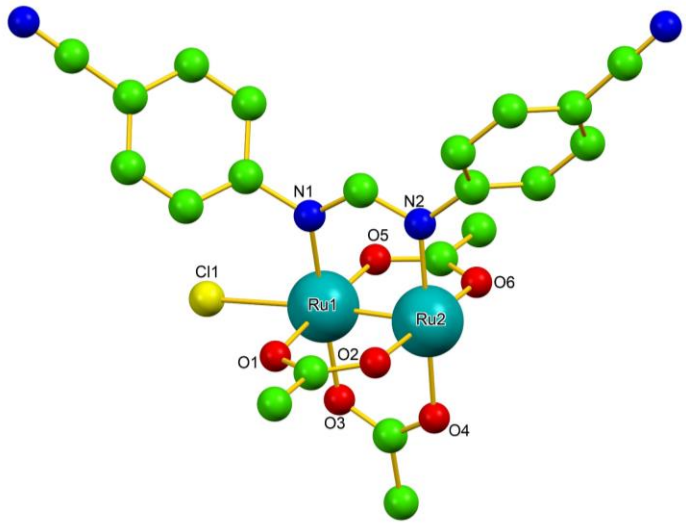
Table S1. Data collection and refinement statistics.

Compound	**$[Ru_2Cl(D\text{-}p\text{-}CNPhF)(O_2CCH_3)_3]_n$ + RNase A**
PDB code	9FYW
Crystallization conditions	22% PEG4K and 10 mM sodium citrate at pH 5.1
Soaking time	7 days
Data collection	
Space group	*C*2
a (Å)	100.62
b (Å)	32.74
c (Å)	72.25
α/β/γ (°)	90.0/90.29/90.0
Molecules for asymmetric unit	2
Resolution range (Å)	72.25-1.40 (1.53-1.40)
Observations	196542 (3145)
Unique reflections	34804 (960)
Completeness (%)	91.0 (50.4)
Redundancy	5.6 (3.3)
Rmerge (%)	0.048 (0.494)
Average I/σ(I)	19.4 (2.2)
$CC_{1/2}$	0.999 (0.820)
Anom. completeness (%)	89.4 (45.6)
Anom. Multiplicity	2.9 (1.7)
Refinement	
Resolution (Å)	1.40
N° reflections	35176
N° reflections in working set	376
R_{factor}/R_{free}	0.176/0.214
N° non-H atoms in the refin.	2327
Average B-factors (Å²)	
All atoms	19.483
Ru atoms	32.11/25.52
Ru occupancy	0.35
Ramachandran statistics	
Most favoured	201 (95.26 %)
Outliers	3
RMSD bonds (Å)	0.010
RMSD angles (°)	1.756

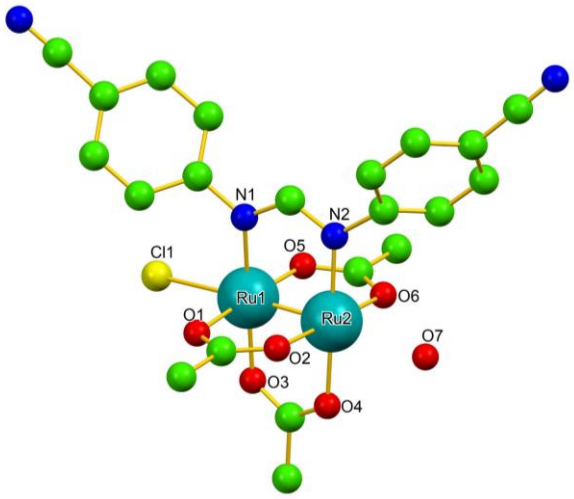
†Rmerge = $\Sigma h \Sigma i \, |I(h,i)-\langle I(h)\rangle| / \Sigma \, h \Sigma i \, I(h,i)$, where I(h,i) is the intensity of the i^{th} measurement of reflection h and $\langle I(h)\rangle$ is the mean value of the intensity of reflection h



$[Ru_2Cl(D\text{-}p\text{-}CNPhF)(O_2CCH_3)_3]$

Atoms	Distance / Å
Ru1-Ru2	2.307
Ru1-Cl1	2.625
Ru1-O1	2.045
Ru1-O3	2.057
Ru1-O5	2.038
Ru1-N1	2.044
Ru2-O2	2.045
Ru2-O4	2.054
Ru2-O6	2.033
Ru2-N2	2.039

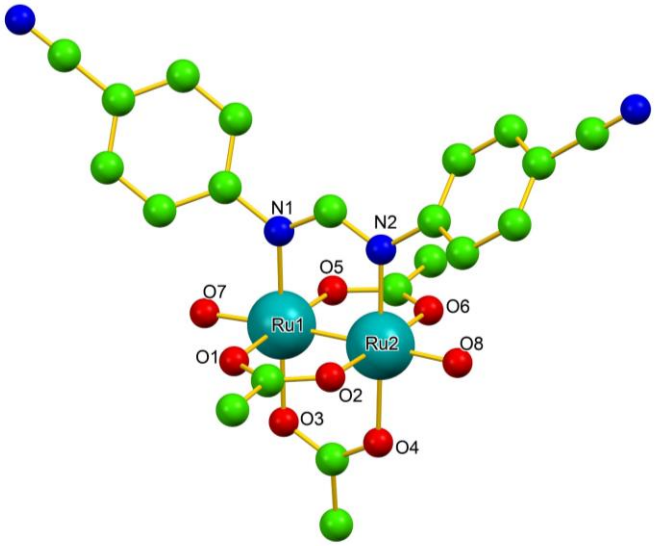
Figure S1. Asymmetric unit representation and selected distances of compound $[Ru_2Cl(D\text{-}p\text{-}CNPhF)(O_2CCH_3)_3]_n$. Hydrogen atoms have been omitted for clarity.



Compound 1

Atoms	Distance / Å
Ru1-Ru2	2.307
Ru1-Cl1	2.635
Ru1-O1	2.033
Ru1-O3	2.054
Ru1-O5	2.042
Ru1-N1	2.039
Ru2-O2	2.038
Ru2-O4	2.057
Ru2-O6	2.045
Ru2-O7	2.625
Ru2-N2	2.044

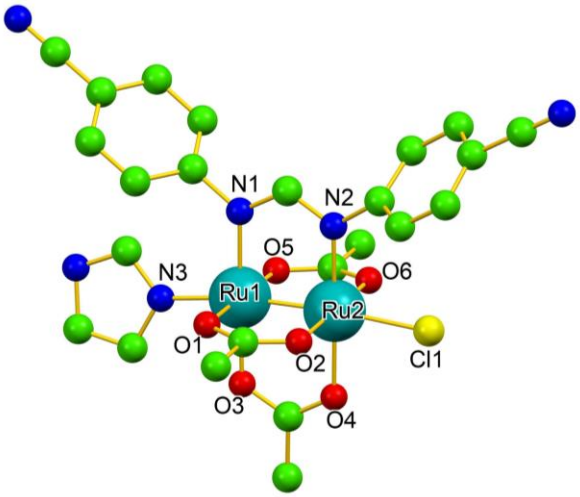
Figure S2. Computational ground state structure and selected distances of complex **1**. Hydrogen atoms have been omitted for clarity. O7 is a water molecule.



Compound 2

Atoms	Distance / Å
Ru1-Ru2	2.307
Ru1-O1	2.105
Ru1-O3	2.122
Ru1-O5	2.089
Ru1-O7	1.773
Ru1-N1	2.068
Ru2-O2	2.078
Ru2-O4	2.126
Ru2-O6	2.112
Ru2-O8	1.777
Ru2-N2	2.068

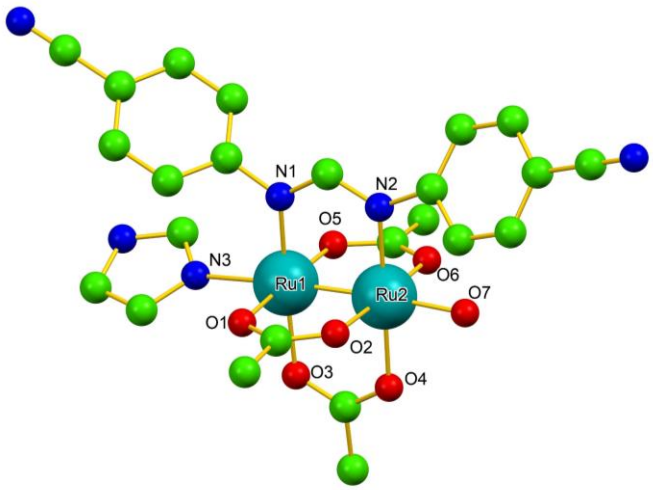
Figure S3. Computational ground state structure and selected distances of complex **2**. Hydrogen atoms have been omitted for clarity. O7 and O8 are water molecules.



Compound 3

Atoms	Distance / Å
Ru1-Ru2	2.293
Ru1-O1	2.022
Ru1-O3	2.039
Ru1-O5	2.037
Ru1-O7	1.773
Ru1-N1	2.017
Ru1-N3	1.940
Ru2-O2	2.049
Ru2-O4	2.066
Ru2-O6	2.019
Ru2-Cl1	2.230
Ru2-N2	2.013

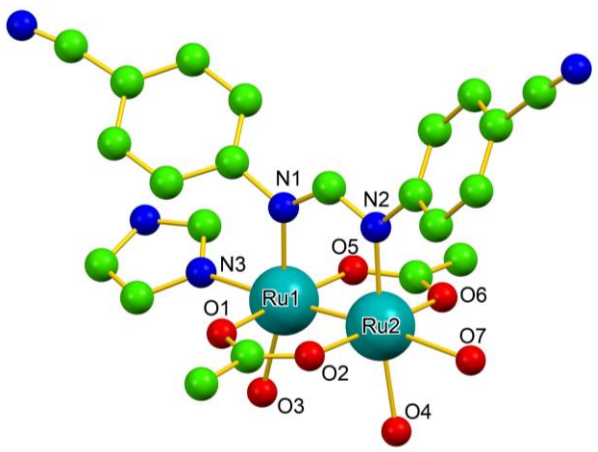
Figure S4. Computational ground state structure and selected distances of complex **3**. Hydrogen atoms have been omitted for clarity.



Compound 4

Atoms	Distance / Å
Ru1-Ru2	2.339
Ru1-O1	2.080
Ru1-O3	2.150
Ru1-O5	2.101
Ru1-N1	2.028
Ru1-N3	2.286
Ru2-O2	2.114
Ru2-O4	2.113
Ru2-O6	2.096
Ru2-O7	1.966
Ru2-N2	2.070

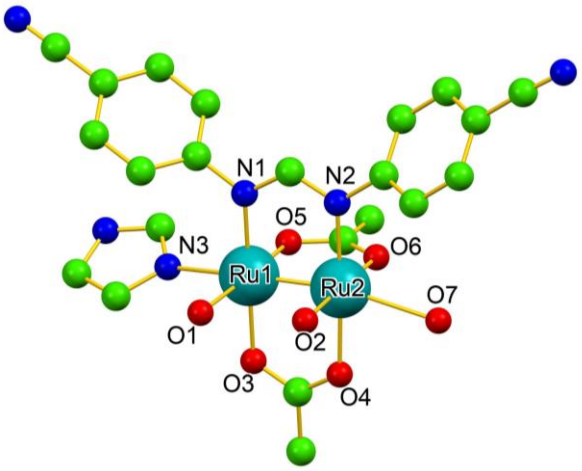
Figure S5. Computational ground state structure and selected distances of complex **4**. Hydrogen atoms have been omitted for clarity. O7 is a water molecule.



Compound 5

Atoms	Distance / Å
Ru1-Ru2	2.428
Ru1-O1	2.077
Ru1-O3	2.203
Ru1-O5	2.097
Ru1-N1	2.041
Ru1-N3	2.369
Ru2-O2	2.124
Ru2-O4	2.202
Ru2-O6	2.099
Ru2-O7	2.351
Ru2-N2	2.115

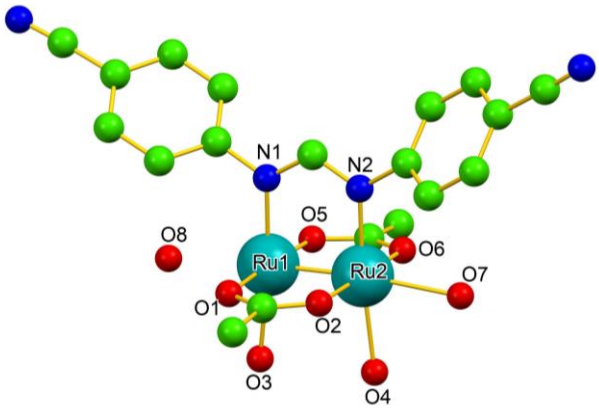
Figure S6. Computational ground state structure and selected distances of complex **5**. Hydrogen atoms have been omitted for clarity. O3, O4, and O7 are water molecules.



Compound 6

Atoms	Distance / Å
Ru1-Ru2	2.319
Ru1-O1	2.156
Ru1-O3	2.121
Ru1-O5	2.053
Ru1-N1	2.042
Ru1-N3	2.320
Ru2-O2	2.185
Ru2-O4	2.141
Ru2-O6	2.073
Ru2-O7	2.489
Ru2-N2	2.083

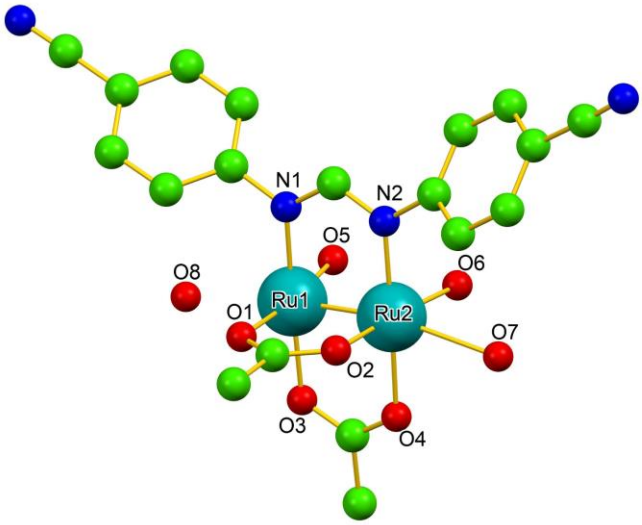
Figure S7. Computational ground state structure and selected distances of complex **6**. Hydrogen atoms have been omitted for clarity. O1, O2, and O7 are water molecules.



Compound 7

Atoms	Distance / Å
Ru1-Ru2	2.336
Ru1-O1	2.082
Ru1-O3	2.236
Ru1-O5	2.094
Ru1-O8	2.612
Ru1-N1	2.031
Ru2-O2	2.091
Ru2-O4	2.230
Ru2-O6	2.098
Ru2-O7	2.408
Ru2-N2	2.029

Figure S8. Computational ground state structure and selected distances of complex **7**. Hydrogen atoms have been omitted for clarity. O3, O4, O7, and O8 are water molecules.



Compound 8

Atoms	Distance / Å
Ru1-Ru2	2.348
Ru1-O1	2.060
Ru1-O3	2.122
Ru1-O5	2.138
Ru1-O8	2.686
Ru1-N1	2.020
Ru2-O2	2.036
Ru2-O4	2.153
Ru2-O6	2.145
Ru2-O7	2.497
Ru2-N2	2.029

Figure S9. Computational ground state structure and selected distances of complex **8**. Hydrogen atoms have been omitted for clarity. O5, O6, O7, and O8 are water molecules.

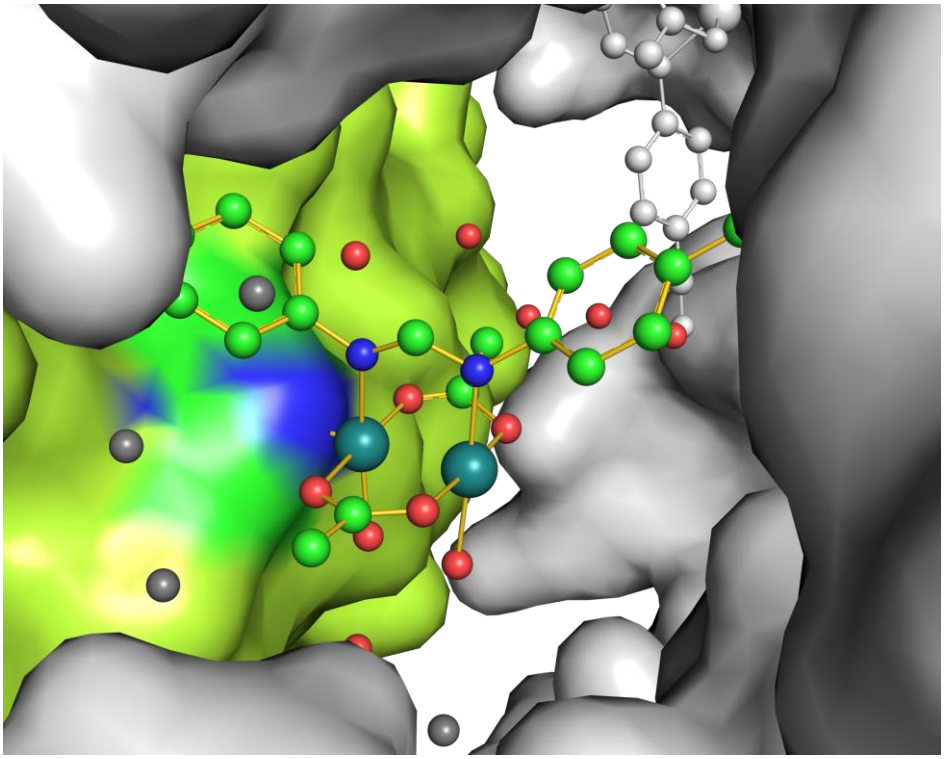


Figure S10. Close-up of the crystal packing in the Ru_2/RNase A adduct. Symmetry mates are in grey. Water molecules are represented as non-bonded grey and red spheres.