Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Photochemical and Thermal Hydrogen Production from Water Catalyzed by Carboxylate-Bridged Dirhodium(II) Complexes

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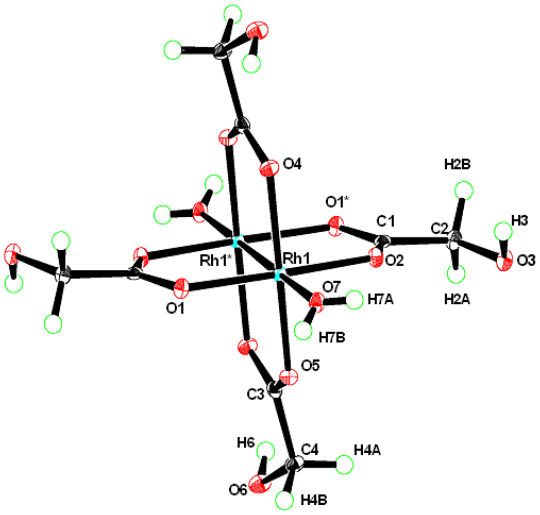

Fig. S1 The molecular structure of **2**, showing the atom-labeling scheme. Displacement thermal ellipsoids are drawn at the 50% probability level. Crystal data for **2**: $C_8H_{16}O_{14}Rh_2$, M = 542.03, Monoclinic, space group $P2(1)/n$, a = 7.755(2), b = 12.509(3), c = 7.990(2) Å, α = 90.00º, β = 108.707(3)º, γ = 90.00º, V = 734.1(3) Å^3, Z = 2, $F(000)$ = 532, D_{calc} = 2.452 gcm^{-3}, μ(Mo K$_\alpha$) = 23.26 cm^{-1}, T = 100 K, radiation = 0.71073 Å, R_1 = 0.0192 for $I > 2.0\sigma(I)$, wR_2 = 0.0469 for all data (1498 reflections), GOF = 0.938 (119 parameters), crystal dimensions 0.12 x 0.03 x 0.01 mm^3. A quality single crystal of **2** (green plate) was mounted on a glass fiber. Diffraction data were measured on a Bruker APEXII CCD-Detector X-ray diffractometer with monochromated Mo K$_\alpha$ radiation from a rotating anode source with a mirror focusing apparatus. The data reduction, structure solution and refinement, and all the necessary computational data processes were performed using APEX2, SAINT, SHELXTL, KENX, and TEXSAN programs. Selected bond lengths [Å] angles [º] for **2**: Rh(1)-Rh(1') 2.3992(7); Rh(1)-O(1), 2.0379(18); Rh(1)-O(2), 2.0409(19); Rh(1)-O(4), 2.0419(18); Rh(1)-O(5), 2.0346(18); Rh(1)-O(7), 2.299(2); O(5)-Rh(1)-O(1), 93.38(7); O(5)-Rh(1)-O(4), 176.04(7); O(1)-Rh(1)-O(4), 87.29(7); O(5)-Rh(1)-O(7), 94.18(7); O(4)-Rh(1)-O(7), 89.71(7); O(5)-Rh(1)-Rh(1'), 87.72(5); O(4)-Rh(1)-Rh(1'), 88.41(5); O(7)-Rh(1)-Rh(1') 177.61(5).

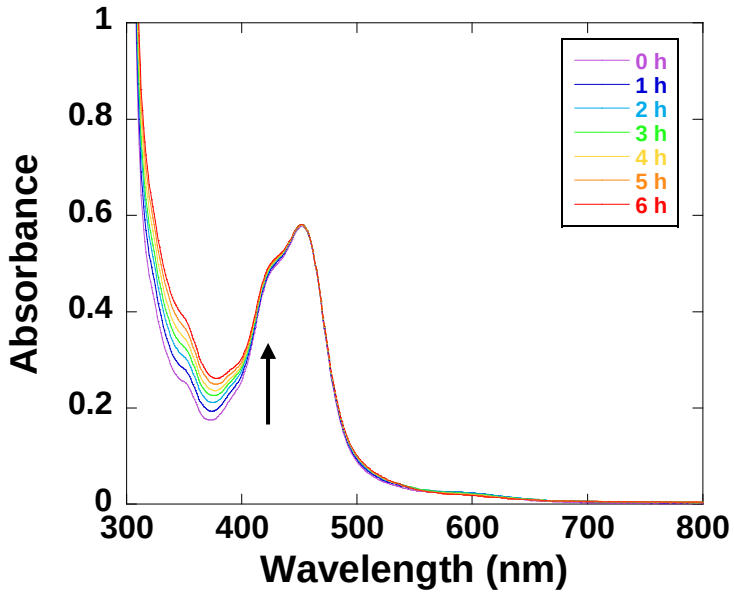

Fig. S2 Spectral changes during the photochemical H_2 production from an aqueous acetate buffer solution (0.03 M CH_3CO_2H and 0.07 M CH_3CO_2Na, pH = 5.0; 10 mL) containing EDTA (30 mM), $MV(NO_3)_2$ (2 mM), $[Ru(bpy)_3](NO_3)_2 \cdot 3H_2O$ (0.04 mM), and $[Rh_2(\mu\text{-gly})_4(H_2O)_2]$ (**2**) (0.1 mM), in Ar at 20 °C (irradiation with 300 W Xe). The spectra were monitored every 1 h up to 6 h of irradiation.

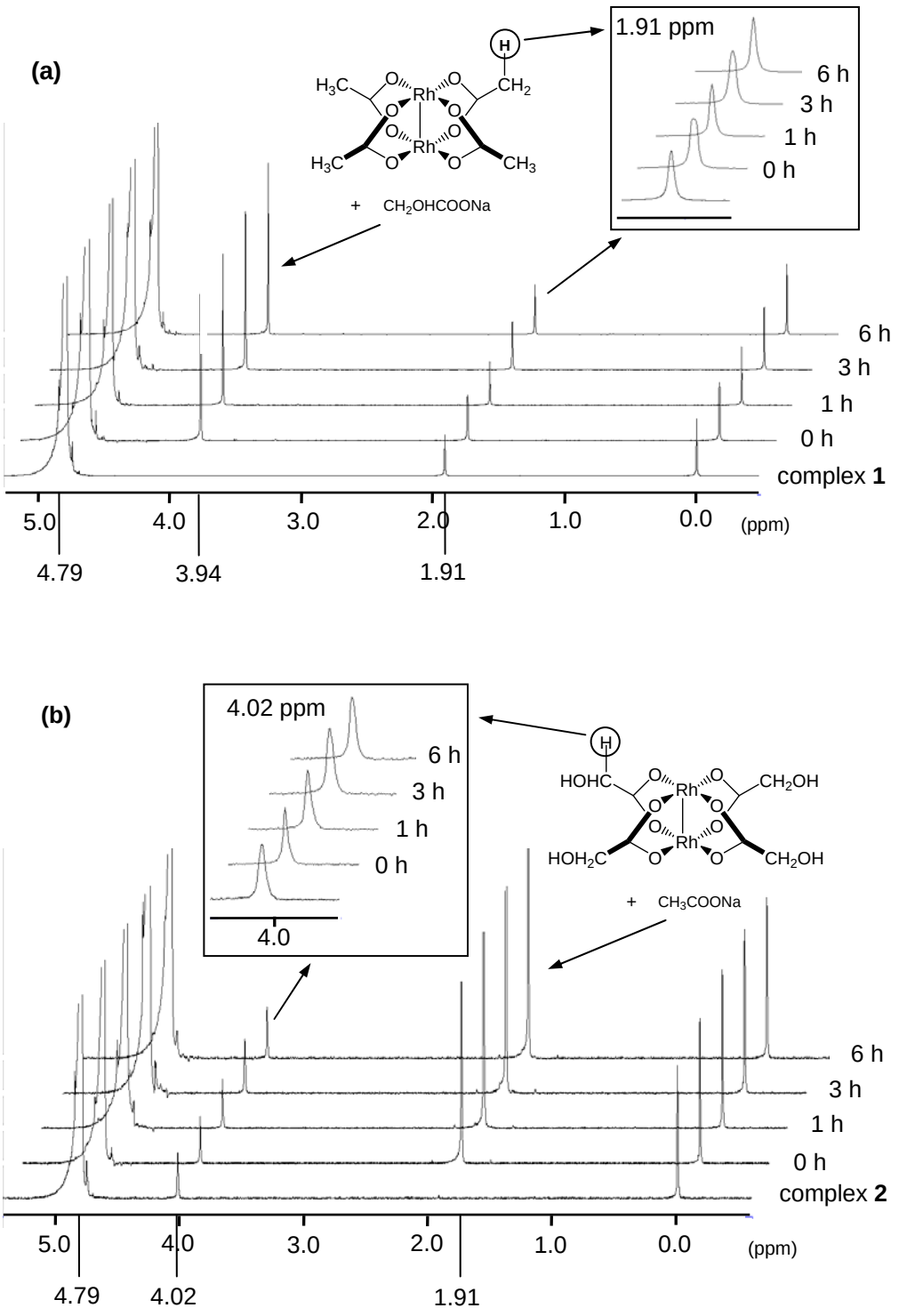

Fig. S3 The time course of ^{1}H NMR spectra (in D_2O) of (a) $[Rh_2(\mu\text{-}OAc)_4(H_2O)_2]$ (**1**) in the presence of 18 equiv. of sodium glycolate and (b) $[Rh_2(\mu\text{-}gly)_4(H_2O)_2]$ (**2**) in the presence of 24 equiv. of sodium acetate at room temperature.

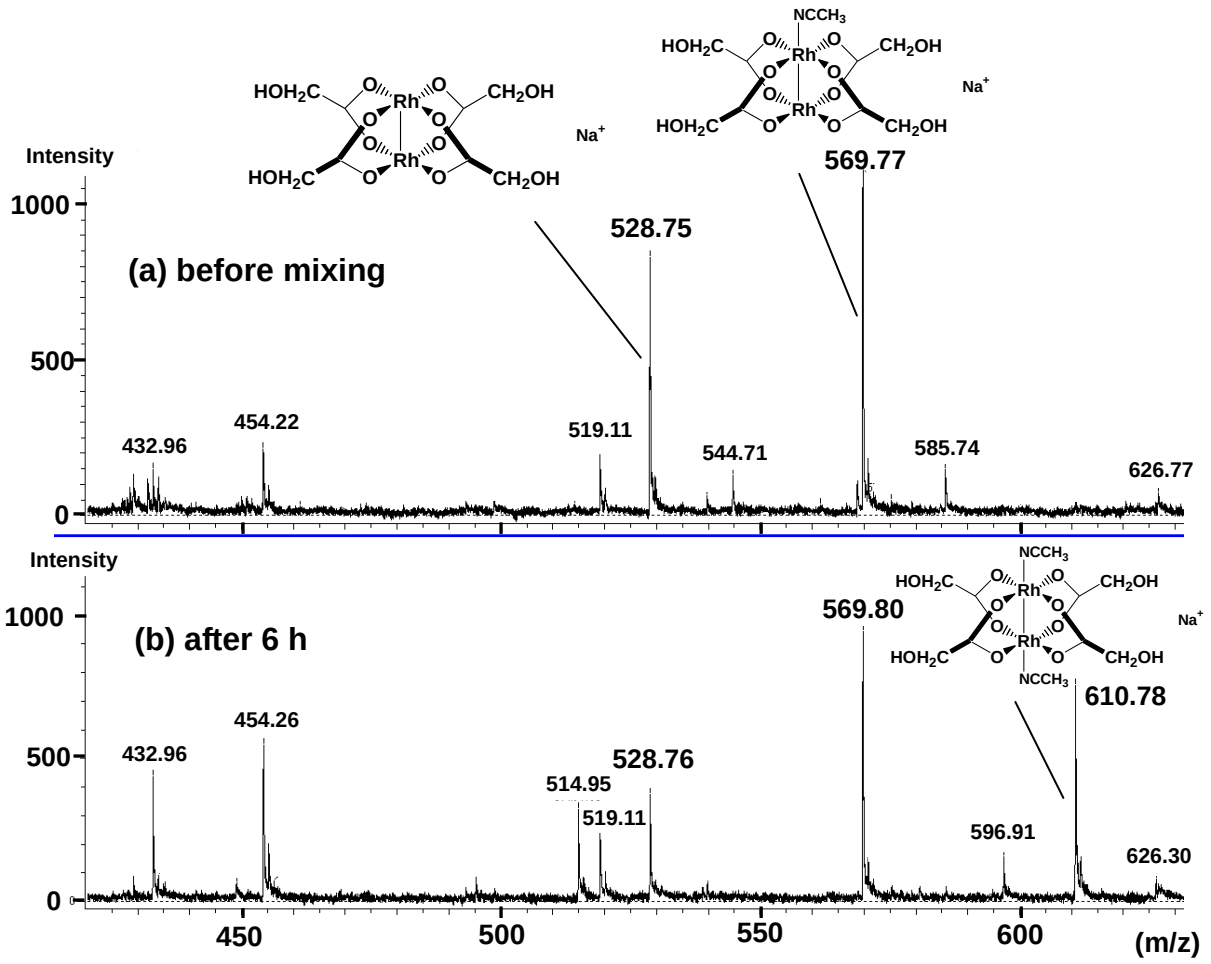

Fig. S4 The time course of ESI-TOF mass spectra of $[Rh_2(\mu\text{-gly})_4(H_2O)_2]$ (**2**) (0.52 mM) in a 2:1 water/acetonitrile mixture in the absence (a) and the presence (b) of sodium acetate (5.2 mM). The spectrum (b) was measured at 6 h after adding sodium acetate. As far as the reported photolysis conditions are concerned, substitution of bridging carboxylates by the free carboxylate via a thermal reaction can be ruled out. This observation confirms that solvolysis of carboxylate bridges in aqueous media is negligible.

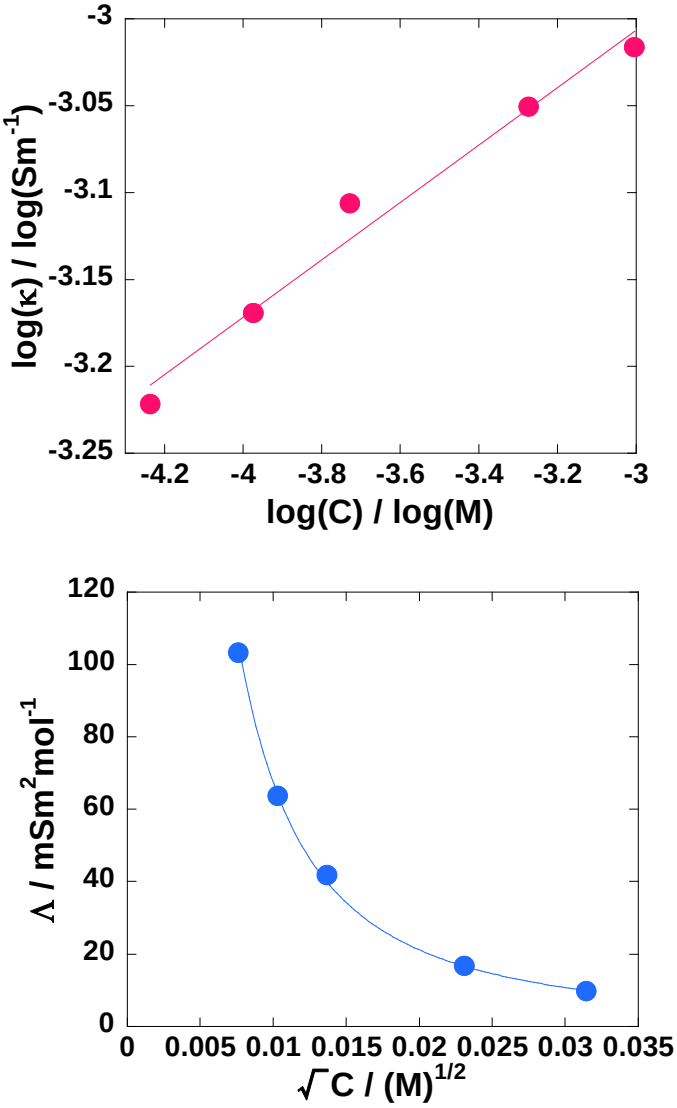

Fig. S5 The specific conductivity (log(κ)) of aqueous solutions of $[Rh_2(\mu\text{-}OAc)_4(H_2O)_2]$ (**1**) as a function of the molar concentration (log(C)) (top), and the corresponding molar conductivity (Λ) as a function of the square root of the molar concentration ($C^{1/2}$) (bottom). The cell constant used in these measurements was determined by use of an aqueous solution of KCl (0.01 M). The conductivity of water used was measured in advance and was subtracted from each conductivity.

$$[Rh_2(\mu\text{-}OAc)_4(H_2O)_2] \underset{}{\overset{K_{a1}}{\rightleftharpoons}} [Rh_2(\mu\text{-}OAc)_4(H_2O)(OH)]^- + H^+$$

The pK_{a1} value is roughly estimated as p$K_{a1} \approx 6$ by supposing that the above equilibrium is the only cause for the generation of ionic species in solution. This value is higher than those reported for the aqua ligands bound to a Rh(III) ion (pK_{a1} = 3.45 for $[Rh(OH_2)_6]^{3+}$, G. Laurenczy *et al.*, *Magn. Reson. Chem.*, 1991, **29**, S45; pK_{a1} = 3.41 for *cis*,*cis*-$[(H_2O)(NH_3)_4Rh(\mu\text{-}OH)Rh(NH_3)_4(H_2O)]^{5+}$, F. Christensson *et al.*, *Inorg. Chem.*, 1985, **24**, 2129.).

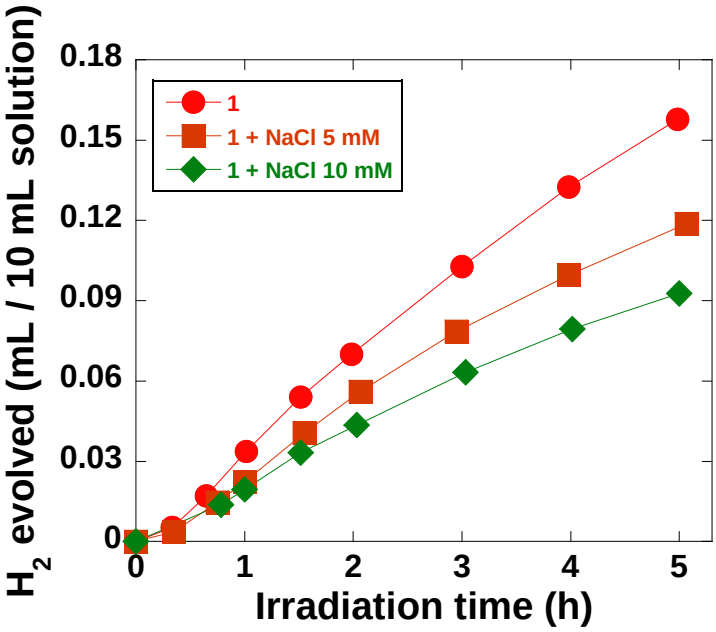

Fig. S6 Dependence of the apparent H_2-evolving activity of the $Rh(II)_2$ complex (**1**) on the chloride ion concentration was examined in the presence of NaCl. Aqueous acetate buffer solutions (0.03 M CH_3CO_2H and 0.07 M CH_3CO_2Na, pH = 5.0; 10 mL) containing EDTA (30 mM), $MV(NO_3)_2$ (2 mM), $[Ru(bpy)_3](NO_3)_2 \cdot 3H_2O$ (0.04 mM), and $[Rh_2(\mu\text{-}OAc)_4(H_2O)_2]$ (**1**) (0.1 mM) was similarly used in the photolysis experiments in the absence and the presence of NaCl (0, 5, and 10 mM as shown above) in Ar at 20 °C (irradiation with 300 W Xe).

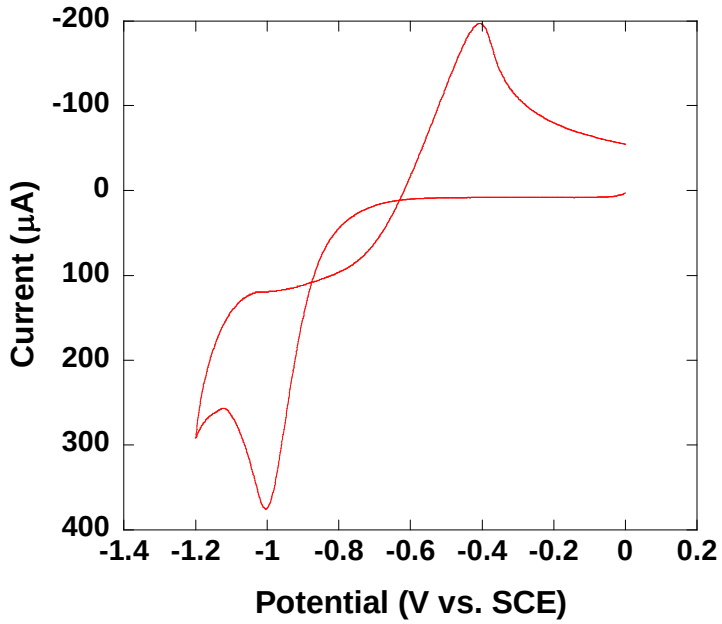

Fig. S7 Cyclic voltammogram of $[Rh_2(\mu\text{-gly})_4(H_2O)_2]$ (**2**) in 0.1 M acetate buffer (0.03 M CH_3CO_2H and 0.07 M CH_3CO_2Na; pH = 5.0) containing 0.1 M KNO_3 at the scan rate of 50 m/V under Ar, where a glassy carbon, a platinum wire, and a saturated calomel electrodes were used as a working, counter, and reference electrodes, respectively.

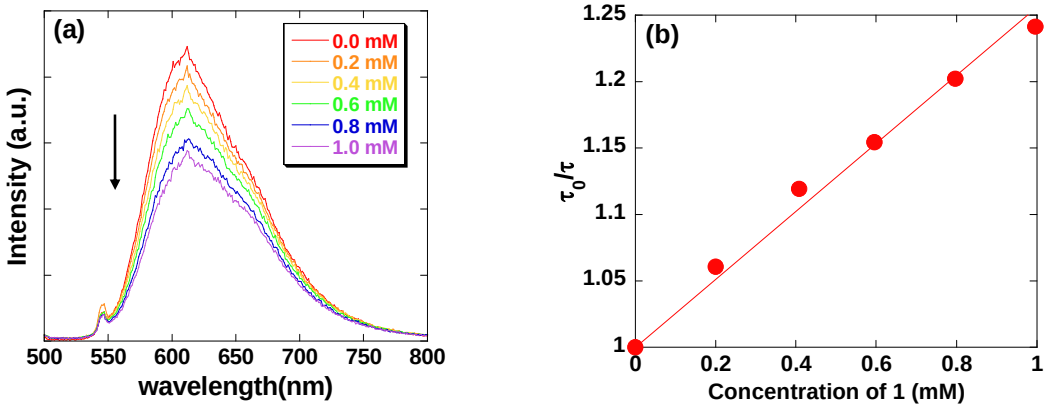

Fig. S8 (a) Luminescence spectra for aqueous solutions of $[Ru(bpy)_3](NO_3)_2 \cdot 3H_2O$ (8.0 μM) in the absence and the presence of $[Rh_2(\mu\text{-}OAc)_4(H_2O)_2]$ (**1**) (0.2-1.0 mM) in Ar at 20 °C. (b) Stern-Volmer plot for the quenching of $Ru^*(bpy)_3^{2+}$ by $[Rh_2(\mu\text{-}OAc)_4(H_2O)_2]$ (**1**), which is plotted using the results of lifetimes determined for the solutions used in (a) (see Fig. S9).

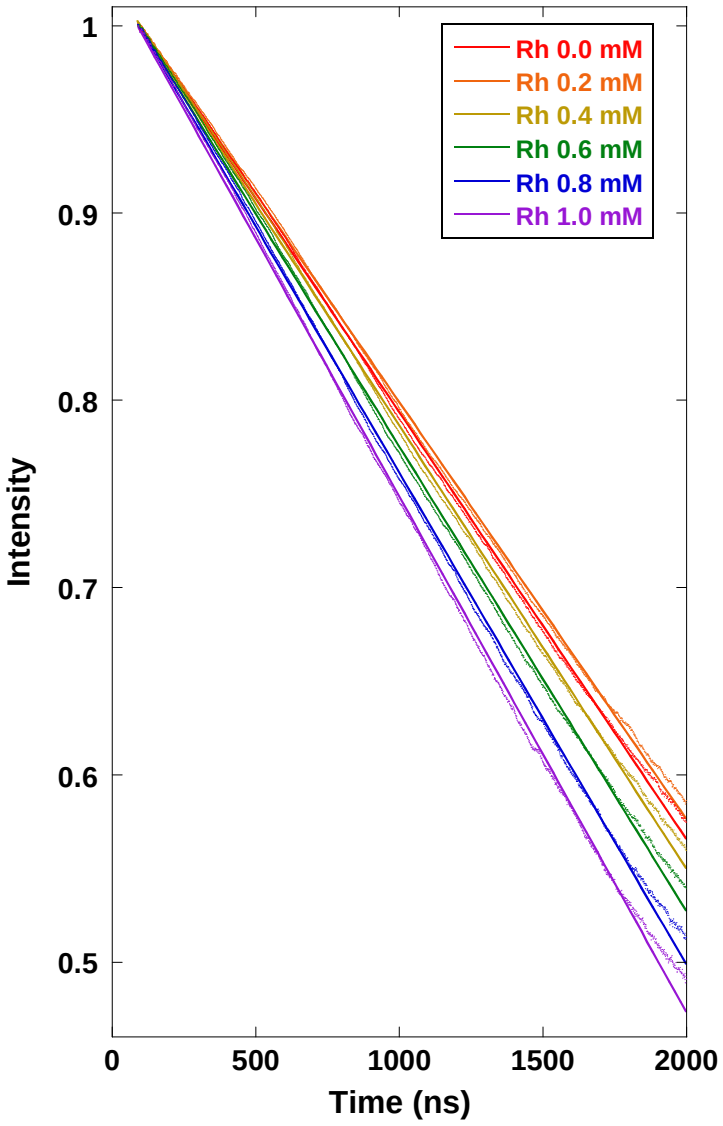

Fig. S9 The logarithmic plots of transient luminescence decay spectra of $Ru^*(bpy)_3^{2+}$ (8.0 μM) monitored at 610 nm in the absence or presence of $[Rh_2(\mu\text{-}OAc)_4(H_2O)_2]$ (**1**) (0.2-1.0 mM) in water under Ar at 20 °C. The least-squares fit of the data gave the lifetimes of 712 ([**1**] = 0.0 mM), 671 ([**1**] = 0.2 mM), 636 ([**1**] = 0.4 mM), 616 ([**1**] = 0.6 mM), 592 ([**1**] = 0.8 mM), and 573 ns ([**1**] = 1.0 mM), respectively.

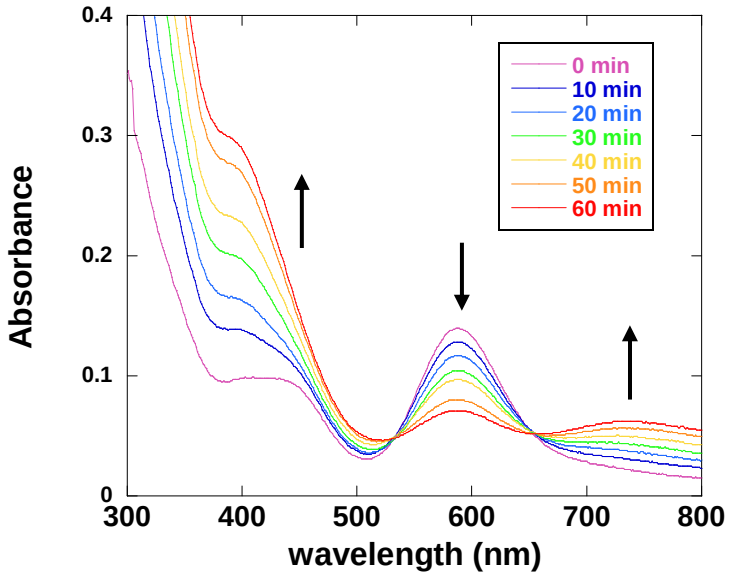

Fig. S10 The time course of UV-visible absorption spectra during the controlled potential electrolysis (i.e., spectroelectrochemistry) at -1.1 V vs. SCE of an aqueous acetate buffer solution (0.03 M CH_3CO_2H and 0.07 M CH_3CO_2Na; pH = 5.0) containing $[Rh_2(\mu\text{-}OAc)_4(H_2O)_2]$ (**1**) (0.65 mM) and KNO_3 (0.1 M) in Ar at 20 °C. The clear isosbestic points observed in these spectra reveal that this is a simple reaction ascribable to the reduction of the $Rh(II)_2$ species into the Rh(I)Rh(II) species, showing that the latter species possesses an absorption bands around 700-800 and 400-500 nm.

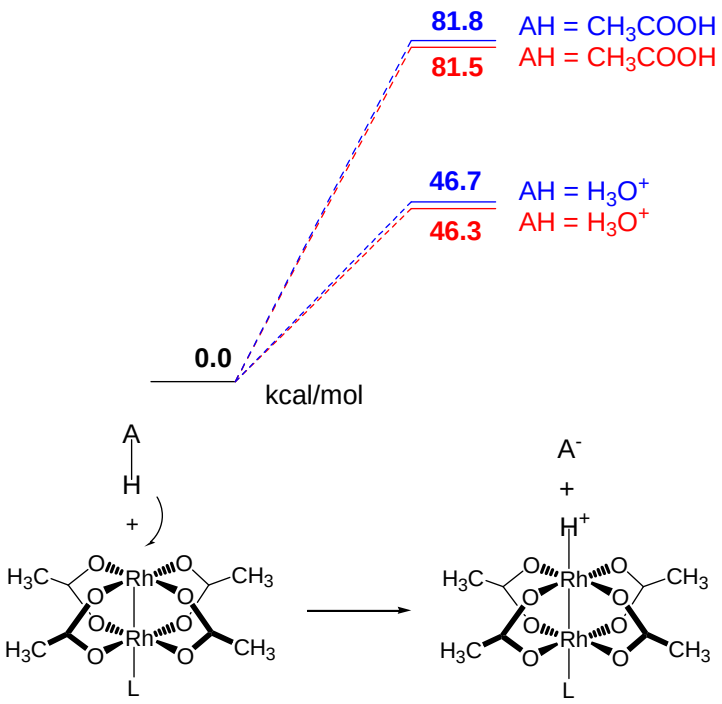

Fig. S11 Relative energies computed for the simple proton transfer processes for $Rh_2(\mu\text{-}OAc)_4(L)$ (L = water; blue lines and L = OAc; red lines) in aqueous media in combination with two kinds of acids (AH = H_3O^+ and CH_3COOH). These processes may be regarded as an oxidative addition of a proton to a dirhodium(II) complex leading to the formation of a dirhodium(III) complex ligated with a hydride ligand, which is also accompanied by the dissociation of a proton from each acid. So the free energy change involves the energy terms arising from the redox process as well as the acid dissociation. Energies of all the chemical species were computed at the B3LYP level of DFT using the LANL2DZ basis set by adopting the polarizable continuum model (PCM) to take the solvation into consideration.

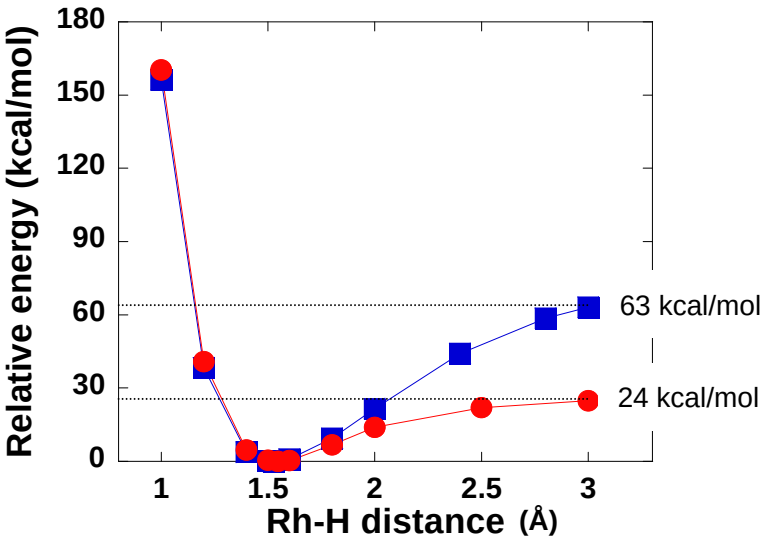

Fig. S12 The DFT-based potential energies computed as a function of the Rh-H distance, calculated at the B3LYP level using the LanL2DZ basis set. The calculations were carried out for $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)] + H^+ + e^-$ (●) at the opened shell electronic state and $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)] + H^+$ (■) at the closed shell electronic state. In the case of the formation of the oxidative addition product $[Rh^{III}_2(\mu\text{-}OAc)_4(H_2O)(H)]^+$, it shows that a stabilization effect of ca. 63 kcal/mol is given by the formation of a Rh-H bond (1.53 Å) (see Fig. S15 and Tables S24-S33). However, it is quite reasonable to consider that the protonation (i.e., oxidative addition of H^+) becomes largely uphill in aqueous media because of the extremely large solvation free energy of H^+ in water, which was previously reported as 259.5 kcal/mol. (C. Lim, D. Bashford and M. Karplus; *J. Phys. Chem.*, 1991, **95**, 5610.)

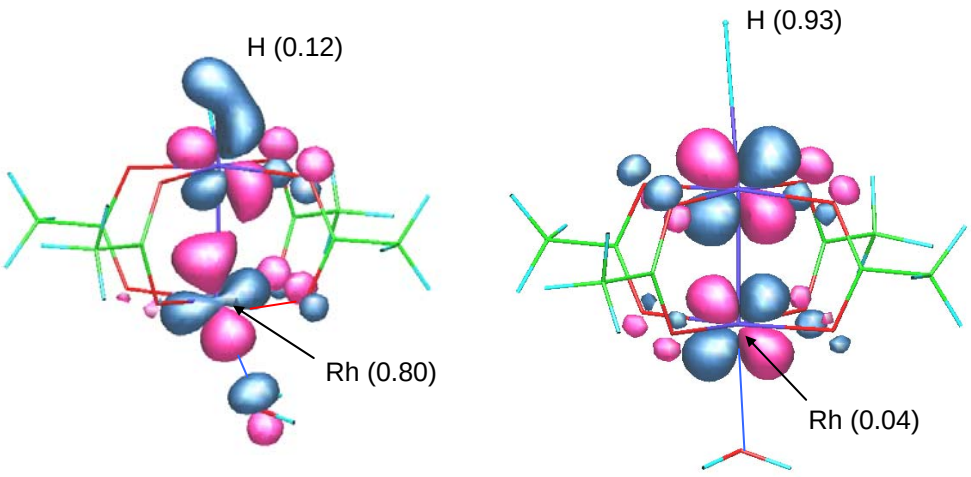

Fig. S13 Spin density of the second highest occupied molecular orbital (HOMO-1) (dπ*) for $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)] + H^+ + e^-$ (i.e., $[Rh^{II}Rh^{III}(\mu\text{-}OAc)_4(H_2O)(H)]$) at different Rh-H distances; 1.55 Å (left) and 3.0 Å (right).

Fig. S14 Structural features of the optimized structures given in Tables S14-S23.

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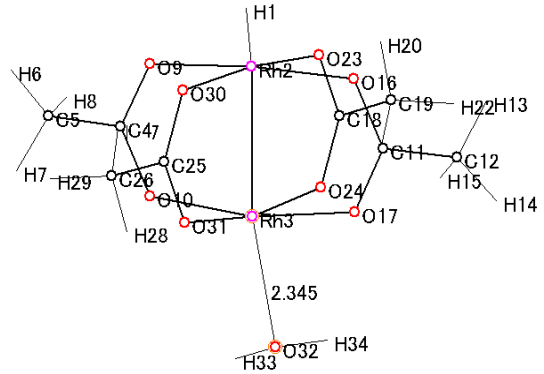
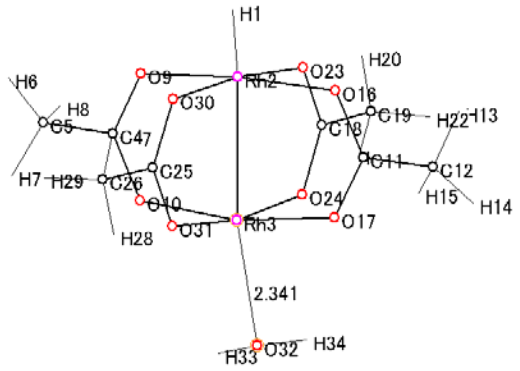
<td> 

$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+{+}e^-$
Rh2-H1=1.00 Å, Corresponding to Table S14
Rh2-Rh3=2.621 Å</td>
<td> 

$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+{+}e^-$
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Rh2-Rh3=2.615 Å</td>
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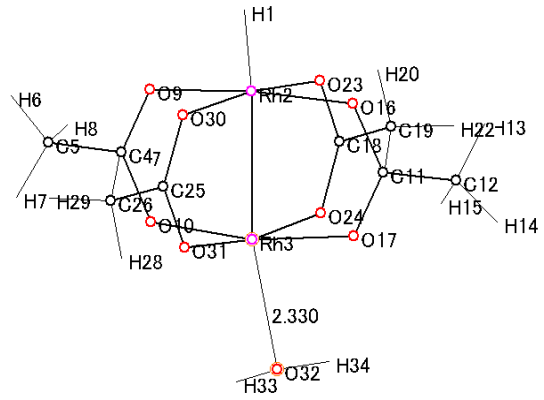
<td> 

$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+{+}e^-$
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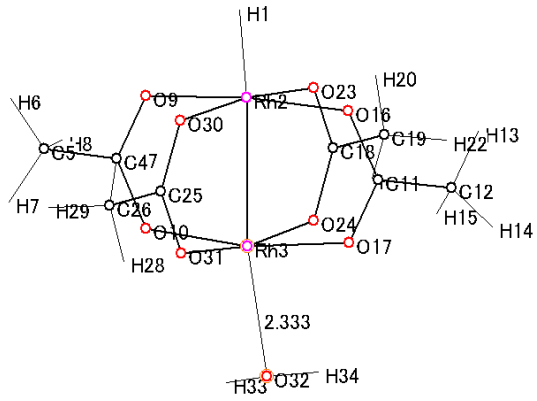
Rh2-Rh3=2.596 Å</td>
<td> 

$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+{+}e^-$
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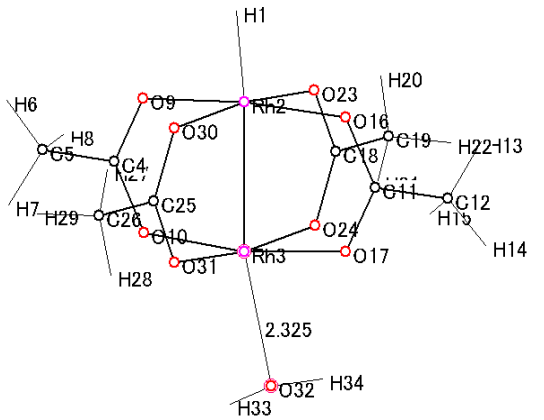
<td> 

$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+{+}e^-$
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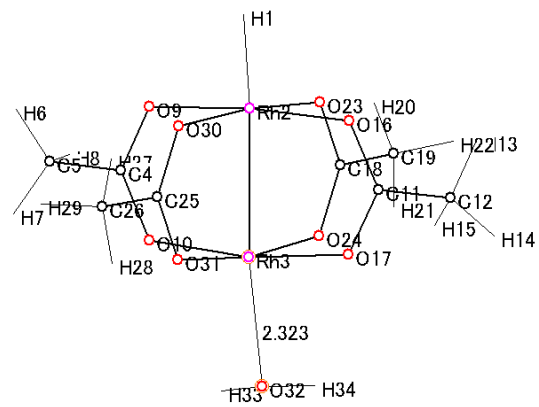
Rh2-Rh3=2.569 Å</td>
<td> 

$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+{+}e^-$
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Rh2-Rh3=2.569 Å</td>
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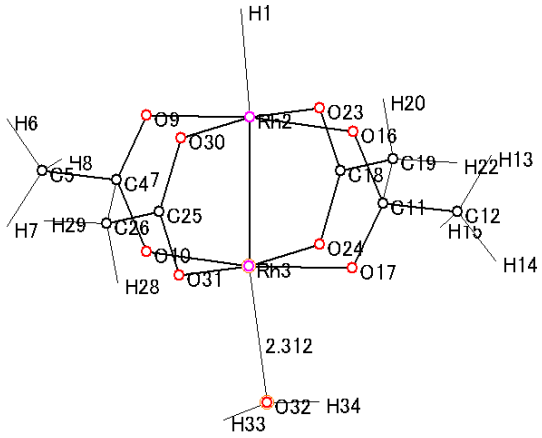
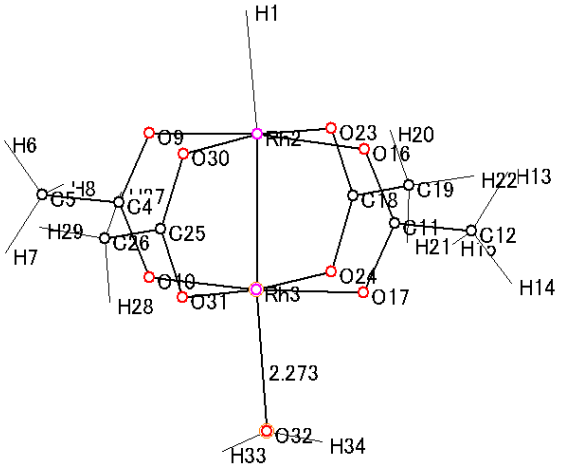
Fig. S14 (continued….)



$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$

Rh2-H1=1.80 Å, Corresponding to Table S20

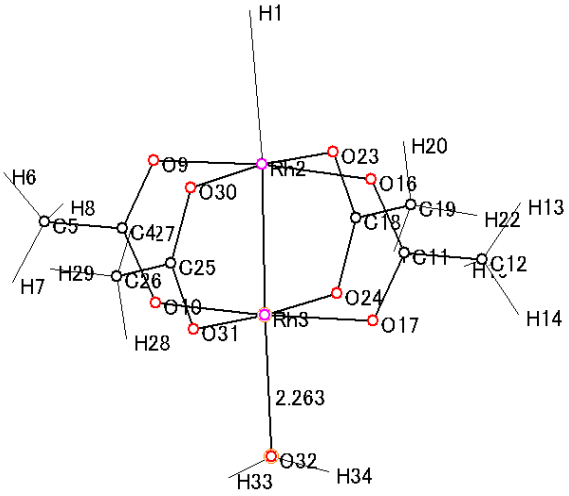
Rh2-Rh3=2.526 Å



$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$

Rh2-H1=2.00 Å, Corresponding to Table S21

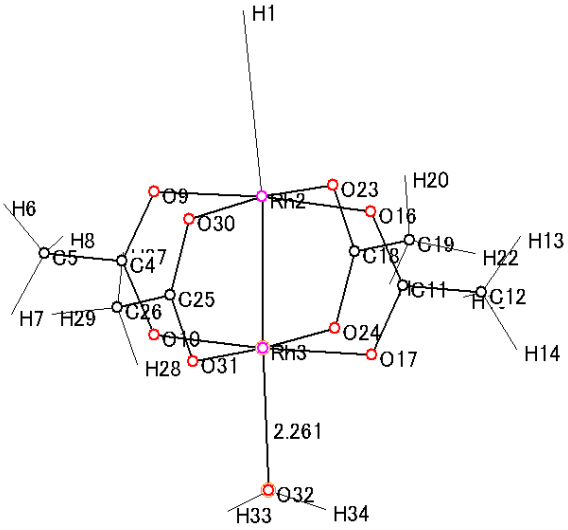
Rh2-Rh3=2.488 Å



$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$

Rh2-H1=2.50 Å, Corresponding to Table S22

Rh2-Rh3=2.446 Å



$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$

Rh2-H1=3.00 Å, Corresponding to Table S23

Rh2-Rh3=2.438 Å

Notes. As summarized in Tables S14-S23, the spin density arising from the doublet character of the system ($[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)] + H^+ + e^-$) can be easily understood by examining the spin density values given in these tables. It shows that the spin density is localized on the Rh ion which is not bound to the H atom when the Rh-H bond is stabilized. On the other hand, the spin density resides on the H atom of interest at the longer Rh-H distances.

Fig. S15 Structural features of the optimized structures given in Tables S24-S33.

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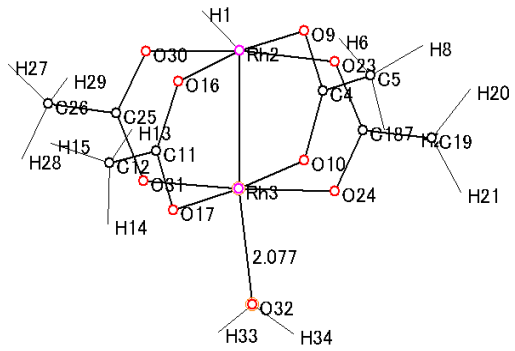
<td> 

$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$
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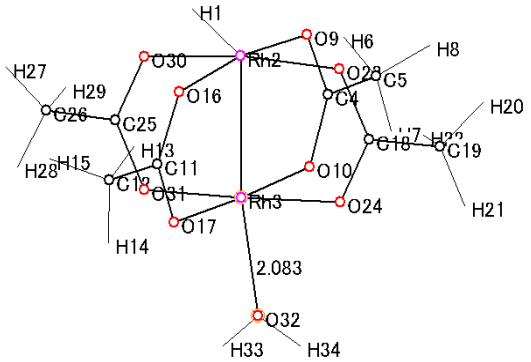
<td> 

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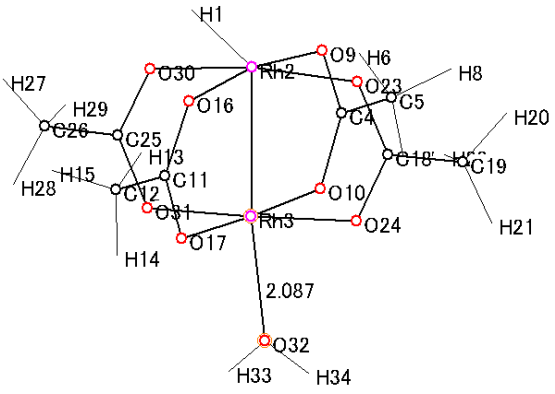
<td> 

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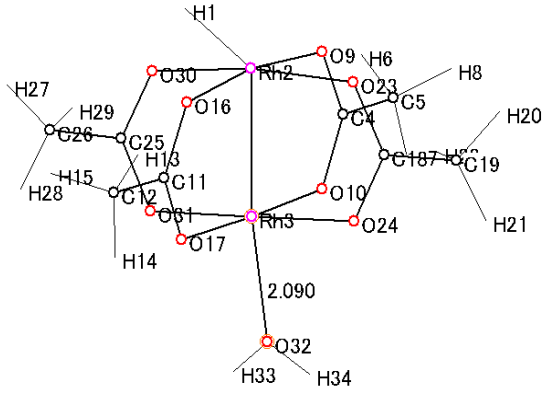
<td> 

$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$
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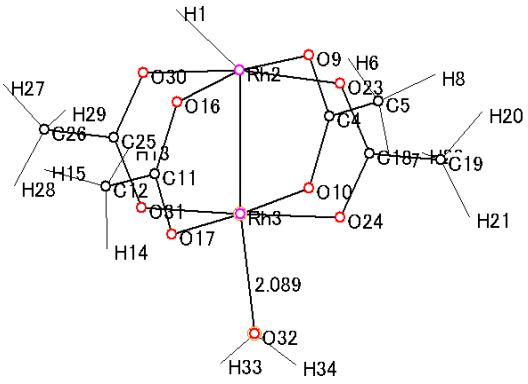
<td> 

$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$
Rh2-H1=1.53 Å
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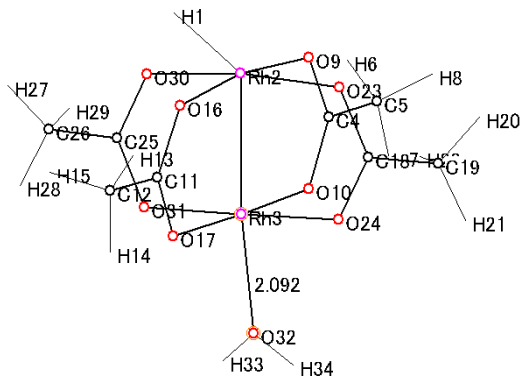
<td> 

$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$
Rh2-H1=1.60 Å
Corresponding to Table S29</td>
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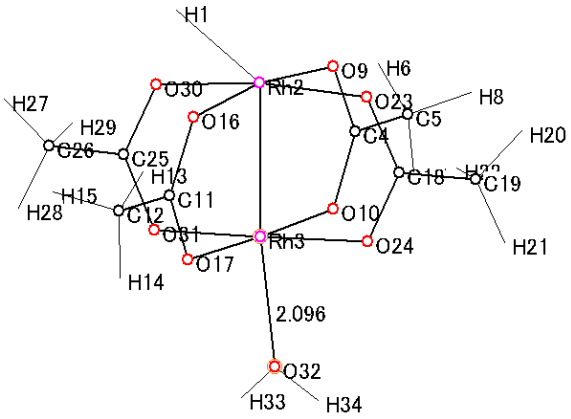
</table>

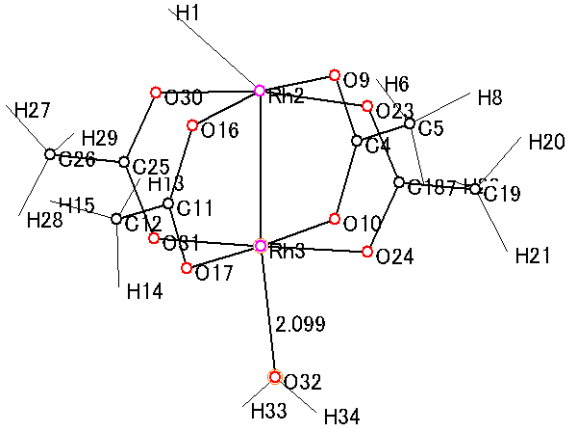
Fig. S15 (continued….)



$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$

Rh2-H1=1.80 Å

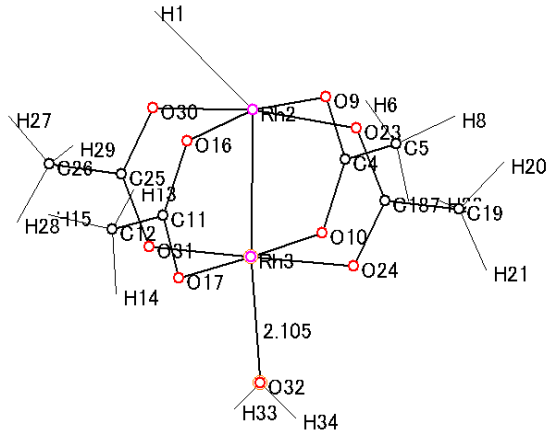
Corresponding to Table S30



$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$

Rh2-H1=2.00 Å

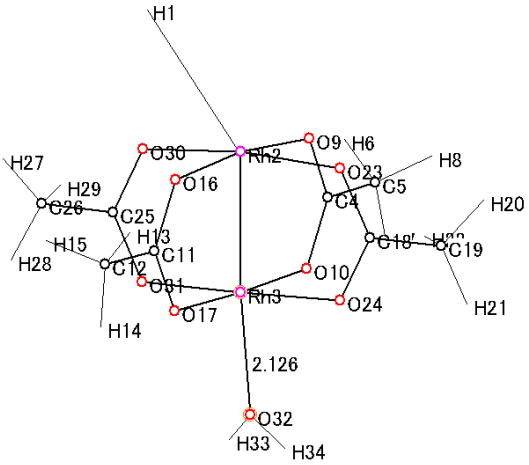
Corresponding to Table S31



$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$

Rh2-H1=2.40 Å

Corresponding to Table S32



$[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$

Rh2-H1=3.00 Å

Corresponding to Table S33

Table S1. Total energies computed for the relevant molecular systems in the gaseous and solvated (water) states. The calculations were carried out at the B3LYP level of DFT using the LANL2DZ basis set. The structures in aqueous media were computed using the polarizable continuum model (PCM) implemented in Gaussian 03 and 09.

Molecular System	ZPVEC	media	Total Energy		Solvation Energy
			hartree	kcal/mol	kcal/mol
$Rh(II)_2(\mu\text{-}OAc)_4(H_2O)$	none	gaseous state	-1209.47219	-758955.8940	
		in water (PCM)	-1209.504414	-758976.1146	-20.22
	applied	gaseous state	-1209.237887	-758808.8665	
		in water (PCM)	-1209.271208	-758829.7757	-20.91
$Rh(II,III)_2(\mu\text{-}OAc)_4(H_2O)(H)$	none	gaseous state	-1210.013951	-759295.8543	
		in water (PCM)	-1210.05096	-759319.0778	-23.22
	applied	gaseous state	-1209.772858	-759144.5661	
		in water (PCM)	-1209.813057	-759169.7914	-25.23
$[Rh(III)_2(\mu\text{-}OAc)_4(H_2O)(H)]^+$	none	gaseous state	-1209.750817	-759130.7352	
		in water (PCM)	-1209.837989	-759185.4364	-54.70
	applied	gaseous state	-1209.508884	-758978.9198	
		in water (PCM)	-1209.598113	-759034.9119	-55.99
$Rh(II)_2(\mu\text{-}OAc)_4(OAc)$	none	gaseous state	-1362.088696	-854724.2778	
		in water (PCM)	-1362.133144	-854752.1690	-27.89
	applied	gaseous state	-1361.816517	-854553.4826	
		in water (PCM)	-1361.861615	-854581.7820	-28.30
$Rh(II,III)_2(\mu\text{-}OAc)_4(OAc)(H)$	none	gaseous state	-1362.659435	-855082.4219	
		in water (PCM)	-1362.686631	-855099.4879	-17.07
	applied	gaseous state	-1362.380406	-854907.3286	
		in water (PCM)	-1362.408812	-854925.1536	-17.83
$[Rh(III)_2(\mu\text{-}OAc)_4(OAc)(H)]^+$	none	gaseous state	-1362.396486	-854917.4191	
		in water (PCM)	-1362.469679	-854963.3480	-45.93
	applied	gaseous state	-1362.115586	-854741.1514	
		in water (PCM)	-1362.189083	-854787.2715	-46.12

ZPVEC denote the zero-point vibrational energy corrections. The solvation energy of atomic hydrogen was considered as zero.

Table S2. Cartesian coordinates of a fully optimized structure of $Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)$ in vacuo. The structure was optimized at B3LYP level of DFT using the LANL2DZ basis set in Gaussian 03.

Atom Label	X	Y	Z
Rh1	0.002067	0.095139	-1.3772
Rh2	-0.00174	-0.0583	1.053364
C3	1.920667	1.877578	-0.04732
C4	2.984594	2.949249	0.01516
H5	3.721367	2.788173	-0.77768
H6	3.465399	2.949327	0.995697
H7	2.519856	3.928827	-0.15458
O8	1.480576	1.530932	-1.22127
O9	1.493175	1.375338	1.076179
C10	-1.92593	-1.8446	-0.26105
C11	-3.03971	-2.86467	-0.31987
H12	-3.02147	-3.38465	-1.2806
H13	-4.00455	-2.35014	-0.22195
H14	-2.94648	-3.57452	0.506652
O15	-1.48629	-1.35228	-1.37763
O16	-1.48321	-1.49901	0.918617
C17	-1.86385	1.934251	-0.05008
C18	-2.88481	3.046622	0.01583
H19	-3.51983	3.025087	-0.8738
H20	-2.36277	4.012026	0.040334
H21	-3.4844	2.955843	0.924881
O22	-1.43595	1.571981	-1.22359
O23	-1.45451	1.417633	1.073947
C24	1.869972	-1.9013	-0.25903
C25	2.946708	-2.96059	-0.31531
H26	2.955182	-3.43507	-1.29915
H27	2.785572	-3.70382	0.470932
H28	3.924063	-2.49125	-0.1435
O29	1.449478	-1.39334	-1.37589
O30	1.437189	-1.54167	0.920215
O31	-0.0078	-0.37163	3.285238
H32	0.79173	-0.86587	3.554225
H33	-0.8257	-0.83447	3.554775

Table S3. Cartesian coordinates of a fully optimized structure of $Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)$ in water. The structure was optimized at B3LYP level of DFT using the LANL2DZ basis set and the PCM method (water) in Gaussian 09.

Atom Label	X	Y	Z
Rh1	-0.00491	0.031337	-1.38258
Rh2	0.003956	-0.02708	1.056957
C3	1.658294	2.119144	-0.11907
C4	2.551812	3.335241	-0.09361
H5	3.16759	3.373366	-0.99551
H6	3.183414	3.325967	0.798153
H7	1.92869	4.238594	-0.06357
O8	1.288096	1.651128	-1.27725
O9	1.280618	1.611408	1.021545
C10	-1.66467	-2.11019	-0.20134
C11	-2.62119	-3.27741	-0.21633
H12	-2.54706	-3.81846	-1.16243
H13	-3.64778	-2.90402	-0.10869
H14	-2.41421	-3.94775	0.622023
O15	-1.29989	-1.59297	-1.33942
O16	-1.26766	-1.66153	0.958107
C17	-2.11485	1.663988	-0.11414
C18	-3.28269	2.619521	-0.08405
H19	-3.85254	2.552886	-1.01379
H20	-2.90678	3.645607	0.019625
H21	-3.92676	2.405046	0.772654
O22	-1.62587	1.323327	-1.27245
O23	-1.63774	1.244198	1.025359
C24	2.117553	-1.65464	-0.19806
C25	3.333771	-2.54788	-0.21504
H26	3.350959	-3.15016	-1.12658
H27	3.345219	-3.19266	0.66727
H28	4.237533	-1.9249	-0.19643
O29	1.619738	-1.26482	-1.33642
O30	1.638591	-1.29624	0.962146
O31	0.031873	-0.10687	3.311883
H32	0.818705	-0.52925	3.709363
H33	-0.78449	-0.41384	3.752875

Table S4. Cartesian coordinates of a fully optimized structure of $Rh^{II,III}_2(\mu\text{-}OAc)_4(H_2O)(H)$ in vacuo. The structure was optimized at UB3LYP level of DFT using the LANL2DZ basis set in Gaussian 03.

Atom Label	X	Y	Z
H1	0.621843	0.017896	-2.87734
Rh2	0.185005	0.003697	-1.3954
Rh3	-0.06591	-0.00188	1.167377
C4	2.008017	-1.81639	0.111299
C5	3.138522	-2.81572	0.210329
H6	3.061968	-3.54716	-0.59942
H7	3.121487	-3.30995	1.183998
H8	4.093936	-2.28783	0.096134
O9	1.674398	-1.41383	-1.08075
O10	1.459473	-1.4116	1.222026
C11	-1.88797	1.826445	-0.40525
C12	-2.98299	2.863795	-0.51275
H13	-3.20123	3.073293	-1.56131
H14	-2.66346	3.784879	-0.01083
H15	-3.88547	2.505646	-0.00475
O16	-1.32513	1.419061	-1.50064
O17	-1.57317	1.407545	0.792015
C18	1.856141	1.969939	0.102497
C19	2.845683	3.109446	0.197736
H20	3.543632	3.071113	-0.64227
H21	3.378641	3.06438	1.150718
H22	2.302068	4.06206	0.150528
O23	1.565341	1.529484	-1.08699
O24	1.346765	1.520911	1.215197
C25	-1.73496	-1.97589	-0.39763
C26	-2.71143	-3.12507	-0.5063
H27	-3.19604	-3.11431	-1.48531
H28	-3.45376	-3.0711	0.2947
H29	-2.16339	-4.07055	-0.40214
O30	-1.21374	-1.52083	-1.49539
O31	-1.45902	-1.52594	0.797493
O32	-1.28127	-0.04735	3.149268
H33	-1.79523	-0.87521	3.036695
H34	-1.85996	0.736307	3.034307

Table S5. Cartesian coordinates of a fully optimized structure of $Rh^{II,III}_2(\mu\text{-}OAc)_4(H_2O)(H)$ in water. The structure was optimized at UB3LYP level of DFT using the LANL2DZ basis set and the PCM method (water) in Gaussian 03.

Atom Label	X	Y	Z
H1	-0.01684	0.322851	-2.93496
Rh2	0.001268	0.017404	-1.40734
Rh3	-0.00436	0.030421	1.151881
C4	1.882997	1.94153	-0.06997
C5	2.91509	3.043242	-0.08192
H6	3.618235	2.894011	-0.90655
H7	3.446976	3.078196	0.871871
H8	2.410567	4.006504	-0.23743
O9	1.46655	1.493023	-1.2227
O10	1.451626	1.518142	1.086418
C11	-1.88552	-1.88684	-0.23695
C12	-2.91941	-2.98603	-0.24532
H13	-3.47	-2.98535	-1.18922
H14	-3.60552	-2.86628	0.598006
H15	-2.41398	-3.95546	-0.13774
O16	-1.4447	-1.45651	-1.39044
O17	-1.47252	-1.44371	0.915869
C18	-1.93669	1.891864	-0.0706
C19	-3.05185	2.909246	-0.08491
H20	-2.95717	3.56403	-0.95564
H21	-3.04413	3.495534	0.837388
H22	-4.01482	2.385266	-0.15543
O23	-1.4965	1.461453	-1.221
O24	-1.49323	1.485853	1.087725
C25	1.932079	-1.83667	-0.2456
C26	3.048354	-2.85192	-0.25199
H27	3.028543	-3.43518	-1.17601
H28	2.967029	-3.50976	0.617837
H29	4.011564	-2.32679	-0.19409
O30	1.47935	-1.42144	-1.40049
O31	1.495014	-1.41281	0.904914
O32	0.033932	-0.50258	3.345272
H33	0.867102	-0.93494	3.661334
H34	-0.7548	-1.00264	3.675206

Table S6. Cartesian coordinates of a fully optimized structure of $[Rh^{III}_2(\mu\text{-}OAc)_4(H_2O)(H)]^+$ in vacuo. The structure was optimized at B3LYP level of DFT using the LANL2DZ basis set in Gaussian 03.

Atom Label	X	Y	Z
H1	0.009129	-0.809142	-2.585841
Rh2	0.007205	0.147133	-1.396389
Rh3	-0.006722	-0.151350	1.053346
C4	1.899493	1.874705	-0.004261
C5	2.975219	2.919846	0.074542
H6	3.817210	2.631237	-0.564735
H7	3.310255	3.044425	1.105500
H8	2.589429	3.871698	-0.309165
O9	1.418948	1.585958	-1.194058
O10	1.472640	1.309877	1.085470
C11	-1.956600	-1.838717	-0.226020
C12	-3.047352	-2.866755	-0.347446
H13	-3.796910	-2.535192	-1.071593
H14	-3.504321	-3.050334	0.626920
H15	-2.617262	-3.805533	-0.719948
O16	-1.563458	-1.237624	-1.322637
O17	-1.449303	-1.596268	0.946422
C18	-1.911678	1.862011	-0.002431
C19	-3.015256	2.877699	0.070344
H20	-2.791695	3.719983	-0.591246
H21	-3.152406	3.220817	1.097472
H22	-3.949033	2.421553	-0.283272
O23	-1.412254	1.585337	-1.184144
O24	-1.490418	1.294449	1.091403
C25	1.973682	-1.821480	-0.194935
C26	3.111807	-2.799407	-0.292104
H27	3.006034	-3.412060	-1.191683
H28	3.148123	-3.426659	0.600880
H29	4.056408	-2.246478	-0.375377
O30	1.577374	-1.237416	-1.297774
O31	1.449124	-1.581386	0.972261
O32	-0.032779	-0.167308	3.142327
H33	0.589761	-0.695659	3.672786
H34	-0.671297	0.368749	3.645951

Table S7. Cartesian coordinates of a fully optimized structure of $[Rh^{III}_2(\mu\text{-}OAc)_4(H_2O)(H)]^+$ in water. The structure was optimized at B3LYP level of DFT using the LANL2DZ basis set and the PCM method (water) in Gaussian 09.

Atom Label	X	Y	Z
H1	0.026142	-0.977970	-2.471797
Rh2	0.012227	0.134259	-1.418673
Rh3	-0.006053	-0.139780	1.055110
C4	1.904133	1.873728	0.016916
C5	2.993650	2.904908	0.099767
H6	3.879913	2.542088	-0.435906
H7	3.249400	3.106888	1.141710
H8	2.665249	3.827721	-0.392556
O9	1.428522	1.588476	-1.175921
O10	1.469863	1.315378	1.105972
C11	-1.980673	-1.815947	-0.227420
C12	-3.098401	-2.814719	-0.338656
H13	-3.917746	-2.392262	-0.930291
H14	-3.454164	-3.097882	0.654097
H15	-2.733510	-3.706844	-0.864137
O16	-1.594493	-1.215305	-1.327892
O17	-1.449036	-1.587600	0.935231
C18	-1.914593	1.858383	0.006622
C19	-3.024742	2.867380	0.082775
H20	-2.802929	3.717536	-0.570375
H21	-3.164564	3.203045	1.112558
H22	-3.955127	2.405458	-0.274444
O23	-1.418682	1.581953	-1.177231
O24	-1.489613	1.298967	1.100534
C25	2.000774	-1.801006	-0.191421
C26	3.122028	-2.797338	-0.285625
H27	2.726322	-3.743517	-0.679170
H28	3.554306	-2.975811	0.701481
H29	3.886632	-2.438013	-0.981166
O30	1.627510	-1.202718	-1.297665
O31	1.448505	-1.576594	0.962256
O32	-0.015840	-0.194047	3.144648
H33	0.585241	-0.837591	3.604735
H34	-0.889981	-0.104781	3.608388

Table S8. Cartesian coordinates of a fully optimized structure of $Rh^{II}_2(\mu\text{-}OAc)_4(OAc)$ in vacuo. The structure was optimized at B3LYP level of DFT using the LANL2DZ basis set in Gaussian 03.

Atom Label	X	Y	Z
Rh1	1.764151	0.394292	0.220458
Rh2	-0.57152	-0.23287	-0.12774
C3	1.034661	-2.23441	1.316208
C4	1.279442	-3.52701	2.06184
H5	2.293352	-3.88527	1.862969
H6	0.539032	-4.27617	1.771531
H7	1.189917	-3.34339	3.140425
O8	2.035057	-1.41354	1.186497
O9	-0.16559	-2.00915	0.866862
C10	0.175387	2.39578	-1.2278
C11	-0.06619	3.687709	-1.97591
H12	0.741142	4.395596	-1.77617
H13	-1.03233	4.110714	-1.68404
H14	-0.10218	3.480355	-3.05302
O15	1.370011	2.169861	-0.76685
O16	-0.82886	1.576934	-1.10544
C17	-0.05268	1.232302	2.373708
C18	-0.42999	1.911478	3.671193
H19	0.46241	2.091833	4.274439
H20	-1.14897	1.295469	4.219951
H21	-0.91145	2.872232	3.448494
O22	1.193867	1.266506	2.007915
O23	-1.00582	0.668275	1.689856
C24	1.258189	-1.06884	-2.27821
C25	1.639153	-1.74881	-3.57396
H26	2.433654	-1.1854	-4.07155
H27	0.764755	-1.84182	-4.22232
H28	2.023165	-2.75327	-3.35382
O29	2.20743	-0.51188	-1.58513
O30	0.007331	-1.09899	-1.92184
O31	-2.68166	-0.96282	-0.44758
C32	-3.83877	-0.54636	-0.31557
O33	-4.06178	0.765776	0.03783
H34	-5.01109	0.99632	0.125434
C35	-5.06176	-1.42089	-0.52344
H36	-5.64577	-1.48828	0.40382
H37	-4.74184	-2.42163	-0.81558
H38	-5.70661	-1.00505	-1.30827

Table S9. Cartesian coordinates of a fully optimized structure of $Rh^{II}_2(\mu\text{-}OAc)_4(OAc)$ in water. The structure was optimized at B3LYP level of DFT using the LANL2DZ basis set and the PCM method (water) in Gaussian 09.

Atom Label	X	Y	Z
Rh1	1.791791	0.333469	0.173399
Rh2	-0.58004	-0.19107	-0.09149
C3	0.93206	-2.15571	1.514474
C4	1.123211	-3.41958	2.316858
H5	1.954509	-3.30215	3.016389
H6	1.360384	-4.24683	1.635434
H7	0.206309	-3.67186	2.855259
O8	1.971566	-1.40116	1.29947
O9	-0.25913	-1.89277	1.054646
C10	0.287795	2.288616	-1.4491
C11	0.11061	3.50181	-2.32938
H12	0.900683	4.231598	-2.13945
H13	-0.87126	3.952329	-2.1602
H14	0.164767	3.19355	-3.38158
O15	1.472841	2.036995	-0.97023
O16	-0.75473	1.536913	-1.2315
C17	0.058954	1.470162	2.270283
C18	-0.26529	2.285199	3.498454
H19	0.644394	2.514805	4.056705
H20	-0.97125	1.74231	4.134362
H21	-0.74389	3.224354	3.193711
O22	1.301554	1.388909	1.888863
O23	-0.9295	0.899361	1.640124
C24	1.166517	-1.32526	-2.18909
C25	1.485531	-2.14566	-3.41508
H26	2.3549	-1.73225	-3.93264
H27	0.624103	-2.17978	-4.08628
H28	1.725666	-3.17206	-3.10849
O29	2.15186	-0.75106	-1.55904
O30	-0.07733	-1.25155	-1.80614
O31	-2.7373	-0.89054	-0.3184
C32	-3.90633	-0.46131	-0.24242
O33	-4.10731	0.880348	-0.0566
H34	-5.05083	1.147592	-0.00279
C35	-5.12489	-1.34824	-0.34197
H36	-5.71621	-1.28262	0.579393
H37	-4.81715	-2.38227	-0.49904
H38	-5.76329	-1.02831	-1.17436

Table S10. Cartesian coordinates of a fully optimized structure of $Rh^{II,III}_2(\mu\text{-}OAc)_4(OAc)(H)$ in vacuo. The structure was optimized at UB3LYP level of DFT using the LANL2DZ basis set in Gaussian 03.

Atom Label	X	Y	Z
H1	3.012058	0.150124	1.489011
Rh2	-0.50386	-0.04034	-0.63004
Rh3	1.598487	0.062043	0.868802
O4	-0.34941	2.034208	-0.75626
O5	-1.48418	0.170429	1.255439
O6	-0.41471	-2.10209	-0.32211
O7	0.751499	-0.22469	-2.26592
O8	1.531154	2.119171	0.589835
O9	0.402051	0.259738	2.555216
O10	1.45917	-1.99995	1.031549
O11	2.628928	-0.14672	-0.91919
C12	0.606625	2.671582	-0.14325
C13	0.629862	4.178726	-0.27086
C14	0.513459	-2.64715	0.409396
C15	0.50869	-4.15321	0.547518
C16	-0.87684	0.271758	2.418732
C17	-1.74215	0.405112	3.649413
C18	2.038952	-0.238	-2.07722
C19	2.928322	-0.37797	-3.29135
C20	-3.72043	-0.09047	-0.98721
O21	-2.5918	-0.14871	-1.54648
O22	-3.87381	0.058032	0.344188
C23	-5.0135	-0.17862	-1.75395
H24	0.280704	4.473677	-1.26411
H25	1.637646	4.556579	-0.08434
H26	-0.05042	4.614498	0.472432
H27	-0.41009	-4.56857	0.129049
H28	0.610893	-4.42908	1.602143
H29	1.372734	-4.5669	0.013221
H30	-2.39864	1.277547	3.551287
H31	-1.11559	0.510956	4.536304
H32	-2.38001	-0.481	3.752196
H33	2.328397	-0.34817	-4.20273
H34	3.471873	-1.32866	-3.23651
H35	3.671321	0.426708	-3.29744
H36	-2.98611	0.120163	0.848232
H37	-5.62096	-1.00067	-1.35911
H38	-5.58372	0.747756	-1.61824
H39	-4.80749	-0.33743	-2.81334

Table S11. Cartesian coordinates of a fully optimized structure of $Rh^{II,III}_2(\mu\text{-}OAc)_4(OAc)(H)$ in water. The structure was optimized at UB3LYP level of DFT using the LANL2DZ basis set and the PCM method (water) in Gaussian 03.

Atom Label	X	Y	Z
H1	2.998768	0.213198	1.500897
Rh2	-0.49685	-0.06786	-0.6223
Rh3	1.585588	0.101646	0.868645
O4	-0.33068	1.99431	-0.86582
O5	-1.47345	0.244977	1.236575
O6	-0.42031	-2.11233	-0.21725
O7	0.753388	-0.34331	-2.25406
O8	1.535702	2.14298	0.487594
O9	0.401272	0.388793	2.541188
O10	1.44412	-1.94866	1.136329
O11	2.623746	-0.20201	-0.90985
C12	0.617348	2.670023	-0.27777
C13	0.637753	4.165981	-0.4721
C14	0.498493	-2.63261	0.546802
C15	0.485558	-4.1252	0.764894
C16	-0.88414	0.403239	2.40186
C17	-1.75313	0.604761	3.614018
C18	2.04516	-0.35386	-2.06956
C19	2.935713	-0.56342	-3.2683
C20	-3.71369	-0.13605	-0.99311
O21	-2.57389	-0.22109	-1.54328
O22	-3.86197	0.079838	0.325393
C23	-4.99785	-0.27034	-1.76081
H24	0.295652	4.419942	-1.47946
H25	1.641697	4.560534	-0.29811
H26	-0.04976	4.631167	0.247458
H27	-0.43421	-4.56213	0.370656
H28	0.581144	-4.34674	1.833371
H29	1.347583	-4.57359	0.254386
H30	-2.40394	1.474997	3.464422
H31	-1.13788	0.754558	4.502826
H32	-2.39684	-0.27231	3.757656
H33	2.34429	-0.58309	-4.18584
H34	3.475652	-1.51248	-3.16064
H35	3.681637	0.237694	-3.31994
H36	-2.97799	0.173197	0.832276
H37	-5.60334	-1.07597	-1.32895
H38	-5.57474	0.658663	-1.67513
H39	-4.79169	-0.48124	-2.81138

Table S12. Cartesian coordinates of a fully optimized structure of $[Rh^{III}_2(\mu\text{-}OAc)_4(OAc)(H)]^+$ in vacuo. The structure was optimized at B3LYP level of DFT using the LANL2DZ basis set in Gaussian 03.

Atom Label	X	Y	Z
H1	2.954538	1.055311	-0.165886
Rh2	-0.524475	-0.336170	-0.347831
Rh3	1.639663	0.598882	0.452046
O4	-0.681735	1.071102	-1.820058
O5	-1.396645	1.020205	1.004780
O6	-0.289760	-1.725929	1.182793
O7	0.415327	-1.603633	-1.628854
O8	1.307593	1.971404	-1.091214
O9	0.604445	1.886525	1.677430
O10	1.651839	-0.765945	1.954185
O11	2.426822	-0.892679	-0.762050
C12	0.275231	1.951899	-1.895224
C13	0.183802	3.026151	-2.944212
C14	0.716834	-1.689479	2.004811
C15	0.831273	-2.738378	3.074145
C16	-0.687556	1.864578	1.727272
C17	-1.405497	2.817695	2.639106
C18	1.712922	-1.651494	-1.558765
C19	2.445883	-2.637122	-2.425193
C20	-3.513887	-0.853278	-0.423204
O21	-2.349006	-1.186454	-0.840956
O22	-3.730545	0.119601	0.456432
C23	-4.728275	-1.569423	-0.928954
H24	-0.432445	2.684089	-3.778709
H25	1.183514	3.304260	-3.286949
H26	-0.284785	3.918487	-2.508760
H27	-0.081247	-3.335002	3.121727
H28	1.032230	-2.264879	4.040717
H29	1.683148	-3.392295	2.849275
H30	-2.103005	3.435407	2.061004
H31	-0.687370	3.456751	3.154623
H32	-1.993803	2.257310	3.375804
H33	1.741056	-3.177652	-3.059044
H34	2.993168	-3.344753	-1.791312
H35	3.183665	-2.111576	-3.041354
H36	-2.907876	0.610025	0.798750
H37	-5.299507	-1.964195	-0.081089
H38	-5.374560	-0.856383	-1.455121
H39	-4.441274	-2.377432	-1.601966

Table S13. Cartesian coordinates of a fully optimized structure of $[Rh^{III}_2(\mu\text{-}OAc)_4(OAc)(H)]^+$ in water. The structure was optimized at B3LYP level of DFT using the LANL2DZ basis set and the PCM method (water) in Gaussian 09.

Atom Label	X	Y	Z
H1	2.922992	1.036743	-0.192303
Rh2	-0.512233	-0.305239	-0.366546
Rh3	1.651099	0.568161	0.511364
O4	-0.598844	1.177225	-1.777157
O5	-1.415821	0.965031	1.015853
O6	-0.356732	-1.788644	1.068320
O7	0.444816	-1.522517	-1.693676
O8	1.320555	2.085645	-0.892254
O9	0.569250	1.750994	1.813721
O10	1.598749	-0.929867	1.912004
O11	2.449729	-0.867709	-0.775546
C12	0.325144	2.091204	-1.745767
C13	0.269736	3.216918	-2.739210
C14	0.643023	-1.828916	1.899609
C15	0.723213	-2.954476	2.889905
C16	-0.726951	1.744423	1.819740
C17	-1.467713	2.639118	2.766583
C18	1.741328	-1.582541	-1.615610
C19	2.481935	-2.512070	-2.533938
C20	-3.520219	-0.798652	-0.538297
O21	-2.351623	-1.098246	-0.973568
O22	-3.739928	0.106523	0.409971
C23	-4.735282	-1.470312	-1.099567
H24	-0.734279	3.302410	-3.158650
H25	0.979249	3.010672	-3.550510
H26	0.566888	4.154260	-2.261354
H27	-0.265849	-3.386063	3.055464
H28	1.149735	-2.598427	3.831152
H29	1.385033	-3.733353	2.489634
H30	-2.102745	3.327644	2.197268
H31	-0.766173	3.205792	3.379618
H32	-2.121379	2.037237	3.407795
H33	1.791987	-3.226419	-2.986295
H34	3.266145	-3.037097	-1.980981
H35	2.963207	-1.924770	-3.325626
H36	-2.915414	0.575549	0.787761
H37	-5.318690	-1.911072	-0.283969
H38	-5.366122	-0.720459	-1.591258
H39	-4.450034	-2.239839	-1.816611

Table S14. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$ with a fixed Rh-H distance (Rh2-H1=1.00 Å) (no charge; doublet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge	Spin Density
H1	0.487402	0.09094	-2.361665	0.32175	0.023963
Rh2	0.18799	0.049159	-1.408457	0.153574	0.03173
Rh3	-0.067392	-0.029961	1.1988	0.410672	0.885637
C4	2.431075	-1.218917	0.119793	0.484904	-0.002935
C5	3.79074	-1.876536	0.211246	-0.710272	-0.001276
H6	3.952698	-2.52691	-0.65252	0.23597	-0.000093
H7	3.874581	-2.438659	1.144178	0.237836	0.000146
H8	4.565217	-1.098685	0.201188	0.237148	-0.000036
O9	2.001014	-0.913003	-1.074004	-0.368661	0.00193
O10	1.79785	-0.983934	1.22994	-0.372441	-0.01172
C11	-2.299754	1.251621	-0.454941	0.487103	-0.003386
C12	-3.6491	1.926238	-0.578611	-0.712699	0.000762
H13	-3.722346	2.446488	-1.535996	0.24439	0.000192
H14	-3.798639	2.623215	0.251101	0.232309	-0.000014
H15	-4.439446	1.165734	-0.531887	0.233382	-0.000119
O16	-1.644718	1.01365	-1.551027	-0.356838	0.003402
O17	-1.89445	0.932422	0.744216	-0.409708	0.012931
C18	1.268583	2.389432	0.088932	0.483973	-0.003144
C19	1.916594	3.754143	0.17801	-0.711178	-0.001007
H20	2.602934	3.900847	-0.659631	0.237099	-0.000176
H21	2.437759	3.858996	1.132815	0.23894	0.000121
H22	1.137022	4.525247	0.123864	0.234072	-0.000014
O23	1.110806	1.885736	-1.105429	-0.36826	0.001656
O24	0.896165	1.828544	1.201061	-0.370243	-0.01058
C25	-1.139955	-2.372356	-0.383121	0.486152	-0.003245
C26	-1.778699	-3.740146	-0.493027	-0.710252	0.000275
H27	-2.204757	-3.877944	-1.489355	0.241228	0.000065
H28	-2.545305	-3.863645	0.277093	0.227449	0.000007
H29	-1.009798	-4.507213	-0.333356	0.238425	-0.000094
O30	-0.755426	-1.802119	-1.486806	-0.3596	0.002696
O31	-1.001456	-1.870165	0.813583	-0.395127	0.005869
O32	-1.305179	-0.220786	3.181551	-0.652899	0.07029
H33	-1.578604	-1.1616	3.183359	0.412916	-0.001612
H34	-2.059365	0.35567	2.931026	0.418885	-0.002221

E(UB+HF-LYP) = -1209.75850427 Hartree

Table S15. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$ with a fixed Rh-H distance (Rh2-H1=1.20 Å) (no charge; doublet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge	Spin Density
H1	0.527797	0.10585	-2.555751	0.147137	0.04353
Rh2	0.185801	0.056672	-1.406568	0.245345	0.026948
Rh3	-0.063561	-0.032792	1.194962	0.440873	0.864952
C4	2.440588	-1.192876	0.120002	0.487216	-0.002706
C5	3.805072	-1.839001	0.213229	-0.710203	-0.001237
H6	3.978843	-2.476813	-0.65746	0.236954	-0.000129
H7	3.887213	-2.411956	1.13978	0.237717	0.000099
H8	4.572523	-1.054175	0.219262	0.237652	-0.000027
O9	2.006205	-0.892366	-1.071554	-0.358185	0.000887
O10	1.805966	-0.960481	1.231764	-0.374312	-0.011315
C11	-2.310461	1.23292	-0.447641	0.492829	-0.002944
C12	-3.660137	1.906571	-0.563532	-0.713348	0.000989
H13	-3.78716	2.322674	-1.5647	0.246371	0.000175
H14	-3.750509	2.693451	0.192111	0.233708	-0.000069
H15	-4.45234	1.169928	-0.378722	0.232209	-0.000117
O16	-1.653858	1.000945	-1.542706	-0.35017	0.003239
O17	-1.899239	0.911684	0.749841	-0.410346	0.014257
C18	1.243815	2.401536	0.101562	0.486795	-0.002904
C19	1.879137	3.77117	0.199582	-0.711209	-0.000976
H20	2.552392	3.935054	-0.645336	0.238253	-0.000215
H21	2.412308	3.8688	1.148593	0.238939	0.000092
H22	1.091532	4.535278	0.166839	0.234155	-0.000002
O23	1.087765	1.903129	-1.093521	-0.35854	0.000892
O24	0.880191	1.82914	1.212768	-0.371966	-0.010942
C25	-1.112924	-2.381882	-0.387194	0.490693	-0.002843
C26	-1.730771	-3.758039	-0.503778	-0.710132	0.000491
H27	-2.207727	-3.873809	-1.479899	0.241943	0.000028
H28	-2.450972	-3.921826	0.302344	0.227209	-0.000022
H29	-0.939107	-4.51335	-0.414698	0.239472	-0.000091
O30	-0.740182	-1.799127	-1.487116	-0.351924	0.002333
O31	-0.976563	-1.881944	0.811531	-0.397802	0.007228
O32	-1.332542	-0.282302	3.145886	-0.651321	0.075025
H33	-1.598559	-1.224682	3.100498	0.414671	-0.002028
H34	-2.084926	0.299164	2.900886	0.419318	-0.002599

E(UB+HF-LYP) = -1209.94886206 Hartree

Table S16. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$ with a fixed Rh-H distance (Rh2-H1=1.40 Å) (no charge; doublet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge	Spin Density
H1	0.542755	0.130465	-2.749405	0.099193	0.076564
Rh2	0.178116	0.05394	-1.399893	0.236868	0.015842
Rh3	-0.058068	-0.029927	1.184181	0.457851	0.838747
C4	2.503829	-1.055057	0.118102	0.489708	-0.002022
C5	3.902375	-1.620971	0.221212	-0.710818	-0.001146
H6	4.115811	-2.253621	-0.644414	0.237866	-0.000162
H7	4.013713	-2.181932	1.152051	0.23757	0.000073
H8	4.623459	-0.793339	0.224348	0.237867	-0.000021
O9	2.053108	-0.790819	-1.073779	-0.349758	0.00023
O10	1.854682	-0.847554	1.228429	-0.37677	-0.010631
C11	-2.377024	1.099088	-0.449663	0.497358	-0.002533
C12	-3.762519	1.693041	-0.571241	-0.714537	0.00124
H13	-3.882549	2.166251	-1.547869	0.247177	0.000144
H14	-3.931993	2.418012	0.23061	0.232975	-0.000095
H15	-4.509855	0.895269	-0.471374	0.23346	-0.000127
O16	-1.707716	0.894271	-1.541273	-0.345276	0.003141
O17	-1.945776	0.808713	0.748837	-0.411741	0.016097
C18	1.106741	2.464202	0.088311	0.489452	-0.002415
C19	1.667718	3.866049	0.179523	-0.712119	-0.000833
H20	2.388802	4.034199	-0.62467	0.238651	-0.00022
H21	2.130053	4.021917	1.157058	0.239373	0.000066
H22	0.849897	4.588714	0.060877	0.234287	0.000001
O23	0.977089	1.951701	-1.102428	-0.35157	0.00035
O24	0.775238	1.877345	1.20349	-0.372079	-0.010806
C25	-0.98133	-2.445123	-0.360104	0.494567	-0.002353
C26	-1.52374	-3.853239	-0.464325	-0.711492	0.000535
H27	-2.015893	-3.994814	-1.429574	0.242386	-0.00002
H28	-2.214574	-4.057453	0.357944	0.227452	-0.000046
H29	-0.689154	-4.563185	-0.396664	0.239687	-0.000082
O30	-0.64403	-1.850374	-1.464306	-0.347708	0.002094
O31	-0.868157	-1.928601	0.834501	-0.395144	0.006344
O32	-1.299466	-0.286062	3.13871	-0.650915	0.076954
H33	-1.508975	-1.24291	3.163323	0.414796	-0.002047
H34	-2.089705	0.234929	2.876431	0.421384	-0.002863

E(UB+HF-LYP) = -1210.00639675 Hartree

Table S17. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$ with a fixed Rh-H distance (Rh2-H1=1.50 Å) (no charge; doublet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge	Spin Density
H1	0.600792	0.053896	-2.837188	0.124038	0.103757
Rh2	0.190843	0.037975	-1.394383	0.199576	0.010689
Rh3	-0.064385	-0.023649	1.174508	0.454454	0.815605
C4	2.268243	-1.490556	0.112461	0.49084	-0.001713
C5	3.539938	-2.301799	0.212878	-0.711013	-0.000936
H6	3.700116	-2.865344	-0.709424	0.238782	-0.000191
H7	3.490549	-2.970765	1.075925	0.236906	0.000039
H8	4.388381	-1.620208	0.355537	0.237854	-0.000004
O9	1.881446	-1.130198	-1.07636	-0.34801	-0.000002
O10	1.661672	-1.181881	1.22397	-0.374799	-0.01076
C11	-2.143545	1.5116	-0.424908	0.498312	-0.002506
C12	-3.399544	2.346409	-0.538565	-0.714116	0.001049
H13	-3.459888	2.801371	-1.529173	0.246793	0.000094
H14	-3.406048	3.117508	0.23812	0.23141	-0.0001
H15	-4.277721	1.706329	-0.385758	0.235438	-0.000112
O16	-1.518861	1.201063	-1.517439	-0.345883	0.00332
O17	-1.771923	1.136665	0.770963	-0.412222	0.013683
C18	1.534491	2.231188	0.10835	0.489943	-0.002002
C19	2.328069	3.514422	0.213623	-0.712564	-0.000793
H20	3.001896	3.610436	-0.64099	0.239543	-0.000245
H21	2.885171	3.533432	1.153975	0.238627	0.00006
H22	1.635833	4.366409	0.207391	0.233985	0.000004
O23	1.315713	1.759817	-1.086028	-0.350549	0.000137
O24	1.102726	1.700195	1.217807	-0.368283	-0.010862
C25	-1.407792	-2.217512	-0.392685	0.49532	-0.002374
C26	-2.197156	-3.502207	-0.507557	-0.712326	0.000732
H27	-2.652404	-3.576098	-1.497714	0.242366	-0.000003
H28	-2.959925	-3.552158	0.274493	0.228236	-0.000065
H29	-1.515728	-4.352345	-0.373221	0.239054	-0.000093
O30	-0.960785	-1.685216	-1.488054	-0.348843	0.002191
O31	-1.205252	-1.737049	0.806001	-0.388373	0.008696
O32	-1.323834	-0.172053	3.132982	-0.651135	0.077931
H33	-1.693972	-1.077139	3.0564	0.413438	-0.002407
H34	-2.011084	0.499996	2.933682	0.423198	-0.002817

E(UB+HF-LYP) = -1210.01305492 Hartree

Table S18. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$ with a fixed Rh-H distance (Rh2-H1=1.55 Å) (no charge; doublet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge	Spin Density
H1	0.621843	0.017896	-2.877344	0.134248	0.124648
Rh2	0.185005	0.003697	-1.395404	0.183218	0.007997
Rh3	-0.065905	-0.001884	1.167377	0.455393	0.799334
C4	2.008017	-1.81639	0.111299	0.491178	-0.001683
C5	3.138522	-2.815724	0.210329	-0.711932	-0.000787
H6	3.061968	-3.547164	-0.599422	0.237219	-0.000113
H7	3.121487	-3.309945	1.183998	0.238486	0.000041
H8	4.093936	-2.287828	0.096134	0.237717	-0.000052
O9	1.674398	-1.413833	-1.080749	-0.347482	-0.00006
O10	1.459473	-1.411595	1.222026	-0.373246	-0.011087
C11	-1.887966	1.826445	-0.405246	0.497308	-0.002445
C12	-2.982985	2.863795	-0.512751	-0.713929	0.000857
H13	-3.201225	3.073293	-1.561308	0.247343	0.000042
H14	-2.663461	3.784879	-0.010826	0.236304	-0.000104
H15	-3.885467	2.505646	-0.004753	0.22873	-0.000085
O16	-1.325128	1.419061	-1.50064	-0.347123	0.003005
O17	-1.57317	1.407545	0.792015	-0.401133	0.010428
C18	1.856141	1.969939	0.102497	0.491057	-0.001676
C19	2.845683	3.109446	0.197736	-0.712118	-0.000748
H20	3.543632	3.071113	-0.64227	0.239948	-0.000245
H21	3.378641	3.06438	1.150718	0.239102	0.000062
H22	2.302068	4.06206	0.150528	0.234155	0.000003
O23	1.565341	1.529484	-1.086989	-0.347548	0.000003
O24	1.346765	1.520911	1.215197	-0.373254	-0.011043
C25	-1.734956	-1.975889	-0.397626	0.496925	-0.002501
C26	-2.711429	-3.125066	-0.506302	-0.711646	0.00085
H27	-3.196039	-3.114305	-1.48531	0.244105	0.000007
H28	-3.453758	-3.071104	0.2947	0.226846	-0.000076
H29	-2.163391	-4.070553	-0.402141	0.239829	-0.000098
O30	-1.213735	-1.520833	-1.495387	-0.346895	0.003044
O31	-1.459019	-1.525936	0.797493	-0.401506	0.010686
O32	-1.281266	-0.047353	3.149268	-0.649259	0.07686
H33	-1.795227	-0.875212	3.036695	0.418973	-0.002533
H34	-1.859959	0.736307	3.034307	0.41899	-0.002534

E(UB+HF-LYP) = -1210.01395087 Hartree

Table S19. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$ with a fixed Rh-H distance (Rh2-H1=1.60 Å) (no charge; doublet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge	Spin Density
H1	0.585283	0.13373	-2.936206	0.142889	0.146745
Rh2	0.16996	0.058075	-1.392904	0.1707	-0.001036
Rh3	-0.057078	-0.027305	1.164417	0.453845	0.785996
C4	2.430831	-1.194727	0.102459	0.491319	-0.001297
C5	3.793655	-1.841596	0.201683	-0.711577	-0.000763
H6	4.020066	-2.384628	-0.718957	0.239271	-0.000192
H7	3.830308	-2.507551	1.06777	0.236559	0.000025
H8	4.551653	-1.059577	0.339199	0.237765	-0.000005
O9	1.992841	-0.896408	-1.084984	-0.345791	-0.000113
O10	1.797594	-0.955235	1.216824	-0.37385	-0.011161
C11	-2.316396	1.24171	-0.406592	0.498181	-0.002573
C12	-3.659967	1.927123	-0.511639	-0.714959	0.001029
H13	-3.803644	2.317824	-1.520719	0.247881	0.000059
H14	-3.723122	2.736105	0.223403	0.23405	-0.000108
H15	-4.457001	1.207107	-0.28725	0.231929	-0.000104
O16	-1.66701	1.005406	-1.503511	-0.346298	0.003392
O17	-1.89577	0.915474	0.78699	-0.403357	0.012439
C18	1.240755	2.400908	0.102668	0.491933	-0.001661
C19	1.885783	3.764999	0.198586	-0.713101	-0.000695
H20	2.73787	3.82158	-0.485534	0.238446	-0.000195
H21	2.201176	3.961473	1.225305	0.24024	0.000054
H22	1.160948	4.529619	-0.108324	0.234736	-0.000007
O23	1.0803	1.900719	-1.088324	-0.347954	-0.000006
O24	0.877063	1.826851	1.215298	-0.37258	-0.011274
C25	-1.120807	-2.380042	-0.383829	0.496209	-0.002385
C26	-1.734504	-3.757107	-0.495781	-0.7115	0.000796
H27	-2.233312	-3.867665	-1.461617	0.243681	-0.000026
H28	-2.435096	-3.930966	0.32528	0.227004	-0.000078
H29	-0.937439	-4.509352	-0.432554	0.240038	-0.000085
O30	-0.755099	-1.7939	-1.481809	-0.34522	0.002288
O31	-0.975838	-1.874768	0.812918	-0.400346	0.008759
O32	-1.22812	-0.350272	3.144716	-0.648932	0.077308
H33	-1.516137	-1.283026	3.048441	0.419028	-0.002434
H34	-1.984998	0.260164	3.013368	0.419762	-0.002694

E(UB+HF-LYP) = -1210.01332315 Hartree

Table S20. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$ with a fixed Rh-H distance (Rh2-H1=1.80 Å) (no charge; doublet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge	Spin Density
H1	0.459082	0.410559	-3.128924	0.142716	0.366262
Rh2	0.097183	0.102298	-1.392835	0.169362	-0.068018
Rh3	-0.019587	-0.034925	1.127101	0.430372	0.646907
C4	2.684499	0.359412	0.08104	0.493746	0.000113
C5	4.177289	0.582172	0.165034	-0.712935	-0.000012
H6	4.666226	0.190327	-0.730353	0.238788	-0.000167
H7	4.577429	0.111722	1.066696	0.236552	-0.000003
H8	4.375257	1.660435	0.222188	0.237458	-0.000015
O9	2.145447	0.332519	-1.102081	-0.346213	-0.000111
O10	2.033435	0.223771	1.203328	-0.367801	-0.012653
C11	-2.618238	-0.285763	-0.356508	0.499094	-0.00296
C12	-4.112078	-0.494497	-0.445233	-0.714335	0.000876
H13	-4.493341	-0.069393	-1.37636	0.246756	-0.000034
H14	-4.609561	-0.043287	0.417828	0.232354	-0.000107
H15	-4.327011	-1.571094	-0.442146	0.235001	-0.000079
O16	-1.95965	-0.141669	-1.465684	-0.349365	0.005386
O17	-2.068018	-0.282529	0.82855	-0.40056	0.008356
C18	-0.328622	2.676968	0.027924	0.491988	-0.000648
C19	-0.561308	4.169168	0.098392	-0.714133	0.000016
H20	-0.09868	4.661616	-0.760461	0.239911	-0.000198
H21	-0.164219	4.565588	1.036316	0.238862	0.000004
H22	-1.640706	4.367318	0.069514	0.233673	-0.000008
O23	-0.185978	2.147224	-1.152099	-0.348247	-0.000063
O24	-0.298207	2.020283	1.153745	-0.364459	-0.011011
C25	0.382497	-2.622309	-0.313093	0.496412	-0.0024
C26	0.616176	-4.113533	-0.395649	-0.712638	0.000703
H27	0.248949	-4.497498	-1.350381	0.243218	-0.00007
H28	0.129381	-4.621983	0.4409	0.228505	-0.000079
H29	1.694536	-4.310479	-0.336771	0.238961	-0.000054
O30	0.346013	-1.956151	-1.427586	-0.349674	0.003728
O31	0.247095	-2.090169	0.872251	-0.386471	0.004486
O32	-0.720561	-0.661995	3.239227	-0.647521	0.065722
H33	-0.376835	-1.56927	3.374338	0.41679	-0.001504
H34	-1.690205	-0.676332	3.087012	0.423833	-0.002362

E(UB+HF-LYP) = -1210.00303289 Hartree

Table S21. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$ with a fixed Rh-H distance (Rh2-H1=2.00 Å) (no charge; doublet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge	Spin Density
H1	0.603309	0.238584	-3.316653	0.11922	0.616225
Rh2	0.106087	0.055591	-1.388109	0.213606	-0.112774
Rh3	-0.039289	-0.025406	1.094553	0.406336	0.451554
C4	2.634261	-0.578181	0.040355	0.491992	0.001021
C5	4.115721	-0.867516	0.120735	-0.714496	0.000585
H6	4.440132	-1.413416	-0.768863	0.237882	-0.000128
H7	4.340662	-1.432137	1.029012	0.235679	-0.000029
H8	4.663826	0.082792	0.159812	0.236816	-0.000013
O9	2.115094	-0.415003	-1.139807	-0.347839	0.00026
O10	1.975905	-0.485258	1.161811	-0.361237	-0.009064
C11	-2.579429	0.607143	-0.303881	0.497899	-0.002715
C12	-4.058014	0.910257	-0.382377	-0.715376	0.0006
H13	-4.281591	1.442732	-1.309742	0.244159	-0.000067
H14	-4.370306	1.497395	0.485582	0.231841	-0.000058
H15	-4.620268	-0.03267	-0.379918	0.234791	-0.000044
O16	-1.916615	0.517362	-1.415166	-0.353734	0.006945
O17	-2.057373	0.427174	0.880388	-0.387172	0.003757
C18	0.602993	2.623409	0.001771	0.491523	0.000249
C19	0.895896	4.105136	0.064548	-0.715769	0.000464
H20	1.65738	4.364925	-0.676553	0.238026	-0.000101
H21	1.222611	4.382558	1.069091	0.23909	-0.000021
H22	-0.016049	4.664189	-0.181341	0.233902	-0.000022
O23	0.551704	2.071145	-1.174724	-0.350384	0.000677
O24	0.400504	1.997384	1.126824	-0.359891	-0.007664
C25	-0.549714	-2.599494	-0.274584	0.496643	-0.001989
C26	-0.83813	-4.081456	-0.34634	-0.714382	0.000598
H27	-1.444955	-4.300237	-1.229313	0.240614	-0.000065
H28	-1.342477	-4.416271	0.563131	0.230116	-0.000057
H29	0.109069	-4.627372	-0.445011	0.238494	-0.000024
O30	-0.356183	-1.967554	-1.391536	-0.352648	0.005137
O31	-0.494005	-2.044983	0.906714	-0.380667	0.002095
O32	-0.615952	-0.274026	3.279135	-0.650372	0.046784
H33	-0.611714	-1.230522	3.486442	0.420724	-0.000775
H34	-1.521694	0.095406	3.333848	0.424615	-0.001341

E(UB+HF-LYP) = -1209.99168661 Hartree

Table S22. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$ with a fixed Rh-H distance (Rh2-H1=2.50 Å) (no charge; doublet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge	Spin Density
H1	0.24972	0.575175	-3.814365	0.08789	0.870778
Rh2	0.036824	0.123176	-1.3648	0.283019	-0.041321
Rh3	-0.018716	-0.063148	1.073054	0.395589	0.148203
C4	2.31473	1.37338	0.01769	0.492106	0.000419
C5	3.599342	2.164854	0.104619	-0.716	0.000306
H6	4.245976	1.921527	-0.743071	0.23606	-0.000029
H7	4.105326	1.960862	1.051117	0.236429	-0.000013
H8	3.365278	3.236182	0.055843	0.236243	-0.000001
O9	1.816439	1.1532	-1.163001	-0.358925	0.001951
O10	1.770925	0.975418	1.132608	-0.356381	-0.001978
C11	-2.302912	-1.327096	-0.284121	0.496168	-0.000626
C12	-3.587904	-2.118721	-0.368503	-0.71621	0.000266
H13	-4.172149	-1.789562	-1.231777	0.241132	-0.000021
H14	-4.163834	-2.007075	0.553582	0.231679	-0.000009
H15	-3.349052	-3.181633	-0.504085	0.234844	-0.000007
O16	-1.758887	-0.928861	-1.391576	-0.356459	0.00302
O17	-1.800219	-1.106259	0.90142	-0.380399	0.000456
C18	-1.35529	2.324737	0.001478	0.492782	0.00022
C19	-2.157716	3.60305	0.082405	-0.716932	0.000281
H20	-2.015003	4.194191	-0.825036	0.239033	-0.000038
H21	-1.863672	4.173601	0.967919	0.237132	-0.000006
H22	-3.22289	3.355222	0.177217	0.233004	-0.000003
O23	-1.007388	1.895531	-1.175414	-0.360263	0.002052
O24	-1.077033	1.715816	1.11954	-0.35633	-0.00185
C25	1.368116	-2.281024	-0.269865	0.496291	-0.000432
C26	2.16607	-3.562559	-0.343806	-0.715669	0.000283
H27	1.905622	-4.11216	-1.252373	0.239725	-0.00002
H28	1.986918	-4.174475	0.543631	0.230443	-0.000012
H29	3.235322	-3.318314	-0.390018	0.237147	-0.000002
O30	1.087104	-1.673695	-1.380245	-0.355547	0.002756
O31	1.024188	-1.845521	0.913123	-0.380757	0.000324
O32	-0.155056	-0.507377	3.288333	-0.652476	0.015487
H33	0.483345	-1.225884	3.473186	0.422853	-0.000197
H34	-1.072982	-0.794649	3.469117	0.422777	-0.000233

E(UB+HF-LYP) = -1209.97869445 Hartree

Table S23. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+ + e^-$ with a fixed Rh-H distance (Rh2-H1=3.00 Å) (no charge; doublet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge	Spin Density
H1	0.827177	0.355576	-4.257595	0.065644	0.927551
Rh2	0.11676	0.07011	-1.356937	0.316639	0.02722
Rh3	-0.065633	-0.041945	1.071973	0.398393	0.036116
C4	2.64663	-0.492547	0.029574	0.492752	0.000271
C5	4.13345	-0.742594	0.128872	-0.715933	0.000091
H6	4.468169	-1.346785	-0.71893	0.235929	-0.000001
H7	4.371169	-1.234056	1.075107	0.236505	-0.00001
H8	4.661926	0.218757	0.090156	0.235898	0.000003
O9	2.137547	-0.314839	-1.153357	-0.361385	0.00156
O10	1.964246	-0.448817	1.138371	-0.356193	-0.000345
C11	-2.603902	0.530977	-0.296748	0.495151	-0.000284
C12	-4.08968	0.790985	-0.395609	-0.715943	0.000072
H13	-4.297902	1.447195	-1.244928	0.24072	-0.000003
H14	-4.461312	1.231049	0.533012	0.231481	-0.000002
H15	-4.611155	-0.159981	-0.565465	0.234886	-0.000004
O16	-1.923276	0.470806	-1.399098	-0.359567	0.001187
O17	-2.091827	0.355258	0.891523	-0.376854	0.000164
C18	0.514132	2.638995	0.0158	0.493413	0.000139
C19	0.750922	4.128692	0.102789	-0.716953	0.000076
H20	1.211214	4.490436	-0.819268	0.2394	-0.000002
H21	1.38182	4.357241	0.966782	0.236573	-0.000003
H22	-0.210771	4.638904	0.242792	0.232751	-0.000002
O23	0.498112	2.090503	-1.162818	-0.362736	0.001369
O24	0.317312	1.993541	1.130965	-0.357086	-0.00034
C25	-0.476276	-2.618897	-0.280529	0.496813	-0.000172
C26	-0.745457	-4.104028	-0.359749	-0.716199	0.000074
H27	-1.106929	-4.366154	-1.356757	0.241498	-0.000003
H28	-1.470467	-4.397374	0.404653	0.229986	-0.000004
H29	0.187644	-4.650803	-0.171533	0.236041	0.000001
O30	-0.262857	-1.975613	-1.385748	-0.358862	0.001189
O31	-0.459318	-2.067134	0.904142	-0.380252	0.000131
O32	-0.459895	-0.295163	3.283864	-0.658039	0.004004
H33	-0.493895	-1.255722	3.466301	0.423801	-0.000026
H34	-1.296701	0.146443	3.529929	0.421728	-0.000016

E(UB+HF-LYP) = -1209.97426491 Hartree

Table S24. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$ with a fixed Rh-H distance (Rh2-H1=1.00 Å) (charge, +1; singlet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge
H1	0.012302	-0.397376	-2.181931	0.342385
Rh2	0.007425	0.182888	-1.367517	0.221546
Rh3	-0.007641	-0.168818	1.05999	0.521956
C4	1.90058	1.88456	-0.008207	0.507829
C5	2.973985	2.930482	0.103815	-0.693779
H6	3.859599	2.608236	-0.456384	0.258855
H7	3.2353	3.097334	1.149953	0.256154
H8	2.625966	3.864531	-0.351528	0.260508
O9	1.448682	1.606258	-1.211158	-0.345659
O10	1.462887	1.308697	1.07481	-0.32956
C11	-1.926006	-1.86143	-0.257977	0.522343
C12	-2.99387	-2.906793	-0.413494	-0.693754
H13	-3.76285	-2.556004	-1.108277	0.259485
H14	-3.43176	-3.149466	0.556423	0.258482
H15	-2.550544	-3.814409	-0.843005	0.259996
O16	-1.511056	-1.244407	-1.337142	-0.354081
O17	-1.449734	-1.617117	0.928713	-0.315526
C18	-1.925022	1.859588	-0.007348	0.51278
C19	-3.029501	2.872803	0.099519	-0.693147
H20	-2.854205	3.692856	-0.602567	0.262502
H21	-3.105911	3.248538	1.121757	0.253137
H22	-3.980566	2.398683	-0.176306	0.25988
O23	-1.452183	1.595907	-1.202276	-0.343456
O24	-1.490815	1.283422	1.080391	-0.349796
C25	1.955377	-1.831859	-0.22169	0.525777
C26	3.075971	-2.823732	-0.352904	-0.692888
H27	2.893301	-3.483281	-1.206826	0.260381
H28	3.179145	-3.404579	0.565362	0.257289
H29	4.013384	-2.287202	-0.547101	0.260526
O30	1.538396	-1.231042	-1.307555	-0.352069
O31	1.455416	-1.594821	0.958377	-0.331669
O32	-0.029748	-0.202733	3.136459	-0.707741
H33	0.567269	-0.76916	3.65703	0.470635
H34	-0.654541	0.343127	3.646894	0.470682

E(RB+HF-LYP) = -1209.50182908 Hartree

Table S25. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$ with a fixed Rh-H distance (Rh2-H1=1.20 Å) (charge, +1; singlet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge
H1	0.008206	-0.551754	-2.342517	0.203106
Rh2	0.013237	0.169819	-1.383712	0.36039
Rh3	-0.008955	-0.165572	1.056635	0.511704
C4	1.899173	1.881319	0.005469	0.510206
C5	2.973326	2.926693	0.109337	-0.693315
H6	3.853536	2.605983	-0.460042	0.259085
H7	3.244019	3.091724	1.153402	0.256575
H8	2.621089	3.861987	-0.340375	0.260586
O9	1.445542	1.594919	-1.195536	-0.349767
O10	1.456918	1.312719	1.088734	-0.325867
C11	-1.93935	-1.850128	-0.249401	0.521254
C12	-3.020952	-2.883302	-0.395969	-0.693619
H13	-3.795925	-2.519554	-1.077278	0.259271
H14	-3.447324	-3.126784	0.57888	0.258299
H15	-2.594072	-3.793027	-0.837378	0.26001
O16	-1.539028	-1.22912	-1.332135	-0.349893
O17	-1.442998	-1.618927	0.930701	-0.314521
C18	-1.919137	1.858104	-0.006401	0.515868
C19	-3.019999	2.8763	0.082182	-0.69269
H20	-2.736996	3.777565	-0.471458	0.26219
H21	-3.23289	3.120621	1.124232	0.253375
H22	-3.924361	2.474696	-0.391733	0.26074
O23	-1.42216	1.599248	-1.193185	-0.347463
O24	-1.500145	1.276715	1.082535	-0.347074
C25	1.966508	-1.826701	-0.208106	0.524068
C26	3.09363	-2.814067	-0.32354	-0.692765
H27	2.968523	-3.423403	-1.223041	0.260206
H28	3.138141	-3.443971	0.567072	0.257321
H29	4.041956	-2.269777	-0.420752	0.259977
O30	1.558043	-1.235284	-1.302381	-0.347527
O31	1.456878	-1.58639	0.96658	-0.331039
O32	-0.059906	-0.190962	3.138377	-0.70761
H33	0.520713	-0.75984	3.67449	0.469257
H34	-0.681661	0.371749	3.63401	0.46966

E(RB+HF-LYP) = -1209.68974780 Hartree

Table S26. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$ with a fixed Rh-H distance (Rh2-H1=1.40 Å) (charge, +1; singlet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge
H1	0.011255	-0.716974	-2.485785	0.217149
Rh2	0.007705	0.158073	-1.392954	0.373141
Rh3	-0.005478	-0.158274	1.054215	0.48647
C4	1.898641	1.877579	0.001943	0.511039
C5	2.975736	2.920675	0.091006	-0.693319
H6	3.824303	2.628102	-0.537819	0.259022
H7	3.299379	3.045751	1.125536	0.256647
H8	2.597647	3.872845	-0.299268	0.260699
O9	1.423451	1.594918	-1.19158	-0.351891
O10	1.470671	1.306314	1.088359	-0.323484
C11	-1.952928	-1.839947	-0.23616	0.520976
C12	-3.041573	-2.868523	-0.367819	-0.693071
H13	-3.796733	-2.526117	-1.081172	0.259071
H14	-3.491722	-3.070511	0.605987	0.25801
H15	-2.611955	-3.799176	-0.760694	0.25949
O16	-1.558525	-1.230298	-1.327866	-0.351491
O17	-1.447438	-1.604244	0.93837	-0.313788
C18	-1.914606	1.859651	0.001288	0.516414
C19	-3.020896	2.871801	0.08395	-0.692829
H20	-2.794179	3.726535	-0.56047	0.262595
H21	-3.166199	3.196015	1.116054	0.253794
H22	-3.950836	2.420428	-0.285452	0.260109
O23	-1.417495	1.592299	-1.183643	-0.349464
O24	-1.491339	1.286193	1.091745	-0.344359
C25	1.973503	-1.820952	-0.203436	0.524327
C26	3.107015	-2.802632	-0.311193	-0.692263
H27	2.99118	-3.41321	-1.211051	0.259849
H28	3.14859	-3.431674	0.580215	0.257376
H29	4.052973	-2.25325	-0.402297	0.259486
O30	1.575141	-1.228701	-1.30144	-0.348904
O31	1.452453	-1.586219	0.966385	-0.330105
O32	-0.039581	-0.18963	3.140579	-0.707445
H33	0.579985	-0.722312	3.670237	0.468269
H34	-0.681949	0.341599	3.644485	0.468481

E(RB+HF-LYP) = -1209.74476260 Hartree

Table S27. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$ with a fixed Rh-H distance (Rh2-H1=1.50 Å) (charge, +1; singlet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge
H1	0.010103	-0.796319	-2.561151	0.270166
Rh2	0.006167	0.148528	-1.396141	0.335384
Rh3	-0.005164	-0.151908	1.053157	0.470341
C4	1.896727	1.87803	-0.004322	0.511195
C5	2.970535	2.925082	0.076075	-0.693217
H6	3.820948	2.629114	-0.548771	0.258926
H7	3.292898	3.061248	1.109576	0.25668
H8	2.589663	3.87198	-0.324112	0.260606
O9	1.41716	1.589078	-1.19424	-0.352755
O10	1.471406	1.311307	1.085201	-0.322631
C11	-1.954747	-1.840266	-0.225631	0.521484
C12	-3.046101	-2.867504	-0.348225	-0.6928
H13	-3.805619	-2.525158	-1.056977	0.258802
H14	-3.490152	-3.066136	0.629105	0.258038
H15	-2.620874	-3.799809	-0.741784	0.259015
O16	-1.563325	-1.237076	-1.32205	-0.351239
O17	-1.445852	-1.59955	0.946159	-0.313574
C18	-1.914413	1.859155	-0.00035	0.516641
C19	-3.018777	2.873873	0.074545	-0.692817
H20	-2.784628	3.727937	-0.56829	0.262446
H21	-3.170575	3.198956	1.105379	0.25393
H22	-3.947117	2.42546	-0.302252	0.260025
O23	-1.413902	1.586136	-1.182499	-0.350668
O24	-1.493437	1.289336	1.092388	-0.343224
C25	1.974927	-1.82036	-0.197591	0.524584
C26	3.111113	-2.800143	-0.298334	-0.691942
H27	2.98789	-3.428943	-1.184645	0.259441
H28	3.163822	-3.411669	0.604579	0.257326
H29	4.053966	-2.249564	-0.410791	0.259197
O30	1.577948	-1.234423	-1.299347	-0.348056
O31	1.451694	-1.581212	0.970192	-0.329889
O32	-0.026025	-0.172394	3.142667	-0.707139
H33	0.607326	-0.691062	3.66987	0.467801
H34	-0.673656	0.349216	3.649771	0.467918

E(RB+HF-LYP) = -1209.75059965 Hartree

Table S28. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$ with a fixed Rh-H distance (Rh2-H1=1.53 Å) (charge, +1; singlet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge
H1	0.009129	-0.809142	-2.585841	0.283231
Rh2	0.007205	0.147133	-1.396389	0.323946
Rh3	-0.006722	-0.15135	1.053346	0.468797
C4	1.899493	1.874705	-0.004261	0.511213
C5	2.975219	2.919846	0.074542	-0.693197
H6	3.81721	2.631237	-0.564735	0.258976
H7	3.310255	3.044425	1.1055	0.256623
H8	2.589429	3.871698	-0.309165	0.260577
O9	1.418948	1.585958	-1.194058	-0.353204
O10	1.47264	1.309877	1.08547	-0.322268
C11	-1.9566	-1.838717	-0.22602	0.521586
C12	-3.047352	-2.866755	-0.347446	-0.692866
H13	-3.79691	-2.535192	-1.071593	0.258788
H14	-3.504321	-3.050334	0.62692	0.258009
H15	-2.617262	-3.805533	-0.719948	0.258923
O16	-1.563458	-1.237624	-1.322637	-0.350672
O17	-1.449303	-1.596268	0.946422	-0.313871
C18	-1.911678	1.862011	-0.002431	0.516816
C19	-3.015256	2.877699	0.070344	-0.692848
H20	-2.791695	3.719983	-0.591246	0.262525
H21	-3.152406	3.220817	1.097472	0.253847
H22	-3.949033	2.421553	-0.283272	0.259972
O23	-1.412254	1.585337	-1.184144	-0.350831
O24	-1.490418	1.294449	1.091403	-0.343394
C25	1.973682	-1.82148	-0.194935	0.524459
C26	3.111807	-2.799407	-0.292104	-0.691993
H27	3.006034	-3.41206	-1.191683	0.259351
H28	3.148123	-3.426659	0.60088	0.257311
H29	4.056408	-2.246478	-0.375377	0.259052
O30	1.577374	-1.237416	-1.297774	-0.34745
O31	1.449124	-1.581386	0.972261	-0.330075
O32	-0.032779	-0.167308	3.142327	-0.707144
H33	0.589761	-0.695659	3.672786	0.467796
H34	-0.671297	0.368749	3.645951	0.468014

E(RB+HF-LYP) = -1209.75081703 Hartree

Table S29. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$ with a fixed Rh-H distance (Rh2-H1=1.60 Å) (charge, +1; singlet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge
H1	0.007303	-0.889795	-2.621644	0.315226
Rh2	0.005718	0.140471	-1.397491	0.304681
Rh3	-0.005368	-0.146255	1.052635	0.45677
C4	1.897522	1.875908	-0.008796	0.512004
C5	2.972806	2.921758	0.065595	-0.693235
H6	3.824181	2.619967	-0.555103	0.258792
H7	3.29311	3.065314	1.098768	0.256673
H8	2.594195	3.866172	-0.342515	0.26055
O9	1.416618	1.580681	-1.196811	-0.353701
O10	1.471896	1.314903	1.083252	-0.3224
C11	-1.96069	-1.8366	-0.21891	0.521501
C12	-3.056097	-2.860489	-0.335444	-0.692582
H13	-3.81283	-2.520437	-1.048259	0.258556
H14	-3.502679	-3.049997	0.642518	0.258053
H15	-2.633895	-3.797509	-0.721058	0.258552
O16	-1.570399	-1.239082	-1.318894	-0.350751
O17	-1.448043	-1.593239	0.950478	-0.313345
C18	-1.911493	1.861313	-0.003555	0.517259
C19	-3.014777	2.877463	0.066209	-0.69287
H20	-2.780401	3.727932	-0.581243	0.262369
H21	-3.165427	3.208194	1.095455	0.254057
H22	-3.943878	2.427861	-0.307273	0.259765
O23	-1.411045	1.580868	-1.184117	-0.351629
O24	-1.490577	1.296615	1.091551	-0.34259
C25	1.977056	-1.819694	-0.191944	0.524428
C26	3.1157	-2.797526	-0.286786	-0.691748
H27	2.995698	-3.429712	-1.171161	0.258833
H28	3.167742	-3.40581	0.618328	0.257357
H29	4.057604	-2.245365	-0.399361	0.25896
O30	1.581838	-1.238848	-1.297142	-0.34718
O31	1.451279	-1.576834	0.973615	-0.329495
O32	-0.024004	-0.165734	3.144234	-0.70736
H33	0.630563	-0.65791	3.670929	0.467186
H34	-0.687723	0.333929	3.652586	0.467312

E(RB+HF-LYP) = -1209.74934193 Hartree

Table S30. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$ with a fixed Rh-H distance (Rh2-H1=1.80 Å) (charge, +1; singlet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge
H1	0.012705	-1.057183	-2.753924	0.345453
Rh2	0.004329	0.128766	-1.399873	0.297853
Rh3	-0.00322	-0.137391	1.051082	0.440303
C4	1.897341	1.875456	-0.015917	0.513543
C5	2.969574	2.924944	0.048037	-0.693081
H6	3.759997	2.693921	-0.673776	0.258951
H7	3.380233	2.987748	1.0572	0.256446
H8	2.545029	3.89616	-0.234803	0.260115
O9	1.407574	1.574383	-1.198559	-0.355282
O10	1.475143	1.321013	1.080323	-0.321731
C11	-1.964008	-1.835733	-0.20767	0.519138
C12	-3.064059	-2.856922	-0.310065	-0.692583
H13	-3.821207	-2.52202	-1.024872	0.257847
H14	-3.50913	-3.032977	0.671111	0.258061
H15	-2.646621	-3.800273	-0.685216	0.25753
O16	-1.575154	-1.250692	-1.314386	-0.349279
O17	-1.447513	-1.583549	0.958117	-0.313506
C18	-1.910605	1.860868	-0.010035	0.518721
C19	-3.013653	2.87772	0.050559	-0.692828
H20	-2.756536	3.743306	-0.568139	0.261982
H21	-3.193968	3.18486	1.08222	0.254129
H22	-3.931547	2.441734	-0.363877	0.259641
O23	-1.40757	1.571146	-1.187144	-0.352932
O24	-1.488075	1.305437	1.088567	-0.342077
C25	1.981341	-1.81851	-0.182047	0.522587
C26	3.124229	-2.793057	-0.266369	-0.69168
H27	3.004786	-3.4384	-1.141331	0.257373
H28	3.180945	-3.388502	0.646953	0.257344
H29	4.063374	-2.238521	-0.389243	0.258706
O30	1.586764	-1.247575	-1.292122	-0.346024
O31	1.453338	-1.568483	0.980947	-0.329293
O32	-0.028631	-0.148521	3.147241	-0.707761
H33	0.631913	-0.625154	3.680638	0.466
H34	-0.697865	0.34955	3.64985	0.466334

E(RB+HF-LYP) = -1209.73578893 Hartree

Table S31. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$ with a fixed Rh-H distance (Rh2-H1=2.00 Å) (charge, +1; singlet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge
H1	0.001704	-1.196631	-2.90783	0.332076
Rh2	0.004101	0.118683	-1.401196	0.32919
Rh3	-0.00545	-0.126216	1.049548	0.433791
C4	1.899626	1.873879	-0.024837	0.515023
C5	2.982345	2.912977	0.028471	-0.69331
H6	3.834515	2.588979	-0.579922	0.258106
H7	3.299186	3.079506	1.059248	0.25678
H8	2.613458	3.84984	-0.405001	0.260372
O9	1.408146	1.562604	-1.203813	-0.356037
O10	1.474119	1.329973	1.075007	-0.320942
C11	-1.966656	-1.834294	-0.194955	0.516808
C12	-3.067189	-2.856645	-0.285464	-0.693218
H13	-3.813344	-2.54122	-1.020176	0.257138
H14	-3.526492	-3.005143	0.693812	0.257917
H15	-2.645348	-3.811053	-0.626354	0.25679
O16	-1.575543	-1.262327	-1.306121	-0.348983
O17	-1.450833	-1.571194	0.969637	-0.315057
C18	-1.908674	1.865781	-0.017545	0.519912
C19	-3.014852	2.87959	0.033331	-0.693018
H20	-2.79262	3.709742	-0.643872	0.261986
H21	-3.153752	3.242176	1.053541	0.25435
H22	-3.947238	2.414507	-0.312052	0.259092
O23	-1.402912	1.565365	-1.190447	-0.353787
O24	-1.487143	1.318191	1.085082	-0.340751
C25	1.977846	-1.82071	-0.172437	0.519485
C26	3.121683	-2.795917	-0.243031	-0.69212
H27	3.02233	-3.430702	-1.127895	0.256282
H28	3.157358	-3.401775	0.664646	0.257265
H29	4.064087	-2.240846	-0.335696	0.257922
O30	1.581213	-1.264651	-1.287738	-0.345278
O31	1.450683	-1.557901	0.989053	-0.330817
O32	-0.017983	-0.125184	3.148839	-0.707926
H33	0.662089	-0.578276	3.67823	0.465409
H34	-0.697977	0.352916	3.656286	0.465549

E(RB+HF-LYP) = -1209.71657892 Hartree

Table S32. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$ with a fixed Rh-H distance (Rh2-H1=2.40 Å) (charge, +1; singlet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge
H1	-0.001108	-1.456438	-3.231986	0.283598
Rh2	0.001931	0.093402	-1.399506	0.397146
Rh3	-0.003416	-0.103958	1.047468	0.434345
C4	1.899642	1.876499	-0.048988	0.517186
C5	2.977306	2.921381	-0.01331	-0.693471
H6	3.827955	2.595538	-0.622846	0.257973
H7	3.299268	3.100951	1.013687	0.256566
H8	2.600769	3.851558	-0.454518	0.260257
O9	1.404854	1.542261	-1.218768	-0.35488
O10	1.475348	1.348483	1.059299	-0.321941
C11	-1.963116	-1.836394	-0.166566	0.514142
C12	-3.060249	-2.864392	-0.232126	-0.694806
H13	-3.786207	-2.591872	-1.003019	0.255859
H14	-3.546054	-2.961068	0.741029	0.257536
H15	-2.627676	-3.835619	-0.505667	0.256059
O16	-1.566054	-1.292156	-1.285717	-0.349617
O17	-1.44997	-1.545872	0.995129	-0.319372
C18	-1.911753	1.865052	-0.040715	0.521159
C19	-3.015768	2.8818	-0.005212	-0.69339
H20	-2.781154	3.711413	-0.679067	0.261418
H21	-3.16724	3.245136	1.012878	0.254562
H22	-3.944804	2.420332	-0.36403	0.258905
O23	-1.403377	1.545014	-1.206302	-0.352598
O24	-1.488677	1.334441	1.069406	-0.339042
C25	1.97452	-1.823	-0.151102	0.516522
C26	3.117459	-2.800685	-0.202212	-0.693582
H27	3.024886	-3.444589	-1.081104	0.254695
H28	3.144304	-3.397267	0.711999	0.257376
H29	4.061835	-2.248266	-0.291077	0.2568
O30	1.566292	-1.296615	-1.27327	-0.346868
O31	1.455852	-1.531327	1.009468	-0.333413
O32	-0.012499	-0.075448	3.152707	-0.707518
H33	0.730436	-0.413078	3.683948	0.464107
H34	-0.730794	0.346468	3.657237	0.464287

E(RB+HF-LYP) = -1209.68049226 Hartree

Table S33. The optimized geometry of $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)]+H^+$ with a fixed Rh-H distance (Rh2-H1=3.00 Å) (charge, +1; singlet), where the optimization was carried out for a gaseous state at the B3LYP level of DFT using the LanL2DZ basis set.

atom	X	Y	Z	Mulliken Charge
H1	0.162497	-1.554959	-3.925779	0.222281
Rh2	0.002178	0.019333	-1.377073	0.437358
Rh3	-0.007111	-0.032328	1.059783	0.459927
C4	1.848109	1.929572	-0.132791	0.51796
C5	2.905544	2.995052	-0.146459	-0.694258
H6	3.75499	2.664384	-0.754919	0.257483
H7	3.235912	3.217513	0.869414	0.256307
H8	2.505767	3.902227	-0.614585	0.259798
O9	1.356358	1.526491	-1.279613	-0.347389
O10	1.433506	1.448212	1.002644	-0.322276
C11	-1.86662	-1.924224	-0.113092	0.51381
C12	-2.897769	-3.017679	-0.136704	-0.696032
H13	-3.714073	-2.746355	-0.813883	0.255844
H14	-3.280361	-3.199617	0.869089	0.258577
H15	-2.443175	-3.93865	-0.522661	0.25509
O16	-1.449089	-1.439684	-1.250706	-0.346313
O17	-1.42642	-1.501046	1.040595	-0.32511
C18	-1.958577	1.8252	-0.126005	0.523121
C19	-3.081703	2.82108	-0.143622	-0.69453
H20	-2.847959	3.632969	-0.839583	0.260993
H21	-3.258417	3.215752	0.858488	0.254577
H22	-3.99512	2.332661	-0.506109	0.25887
O23	-1.454128	1.435007	-1.269484	-0.348043
O24	-1.508165	1.38294	1.014184	-0.33833
C25	1.983215	-1.79944	-0.078602	0.516558
C26	3.112453	-2.792095	-0.083209	-0.695309
H27	3.008852	-3.47726	-0.929103	0.254898
H28	3.13515	-3.343412	0.859142	0.256511
H29	4.064084	-2.257566	-0.200861	0.257359
O30	1.557603	-1.33612	-1.220343	-0.347389
O31	1.484443	-1.424696	1.069148	-0.335794
O32	-0.035681	0.097409	3.181513	-0.708852
H33	0.735881	-0.114807	3.736672	0.460623
H34	-0.777351	0.518967	3.652078	0.461683

E(RB+HF-LYP) = -1209.65015152 Hartree