Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Unprecedented metal-metal bonded $\{Ru_4(\mu_3\text{-}O)_2\}$ butterfly core in oxido-carboxylato bridged mixed valent cluster. Structural elucidation and electronic forms in accessible redox states

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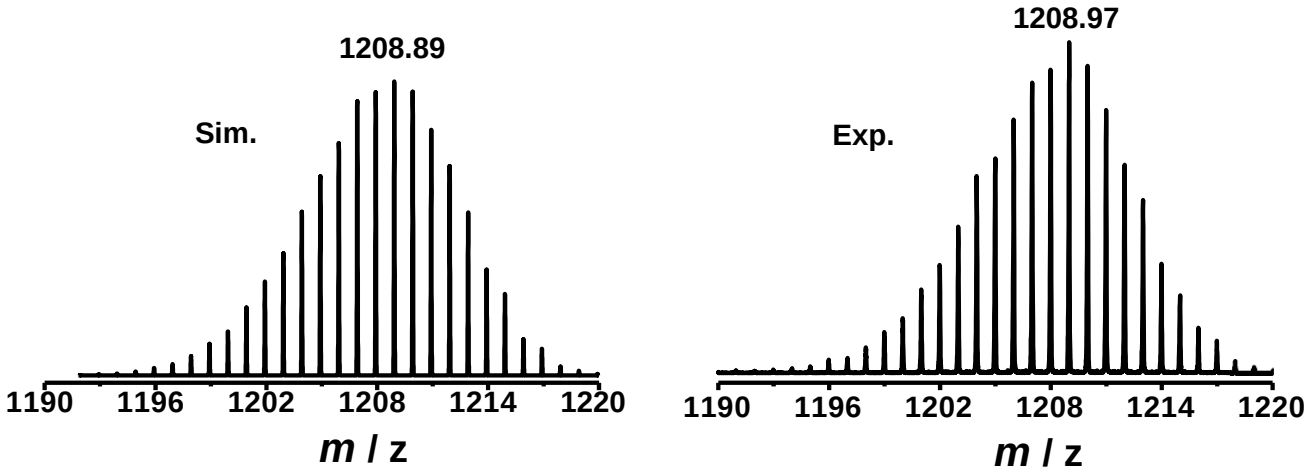


Fig. S1 Experimental and simulated ESI(+) mass spectra of $\{\mathbf{1}\}^{+}$ in CH_3CN

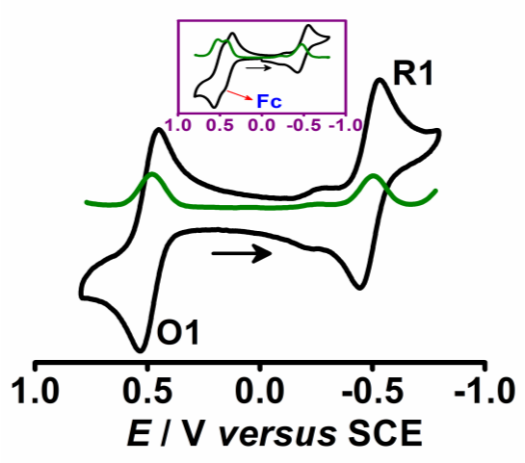


Fig. S2 Cyclic (black) and differential pulse (green) voltammograms of **1** in CH_3CN. Inset shows one-electron transfer process in **1** with reference to ferrocene as an internal standard in CH_3CN

Table S1 Selected crystallographic data for **1**

complex	**1**
empirical formula	C_{36} H_{51} O_{20} Ru_4
formula weight	1208.04
crystal system	triclinic
space group	*C12/C1*
a (Å)	11.8572(3)
b (Å)	13.8306(3)
c (Å)	14.3293(3)
α (deg)	74.4373(18)
β (deg)	89.4963(17)
γ (deg)	80.0332(19)
V (Å^3)	2227.82(9)
Z	2
μ (mm^{-1})	1.405
T (K)	150(2)
D_{calcd} (g cm^{-3})	1.664
F (000)	1206
θ range (deg)	2.330 to 24.998
data/restraints/ parameters	7823 / 0 / 556
R1, *w*R2 [$I > 2\sigma(I)$]	0.0438, 0.0582
R1, *w*R2(all data)	0.0910,0.0990
GOF	1.049
largest diff. peak/hole, (e Å^{-3})	0.741 / -0.759

Table S2 Selected experimental and DFT calculated bond lengths (Å) for **1**

X-ray		DFT
Ru1-O1	1.906(3)	1.907
Ru1-O3	2.078(3)	2.109
Ru1-O9	1.998(3)	2.047
Ru1-O10	2.004(3)	2.056
Ru1-O11	2.011(3)	2.055
Ru1-O12	2.027(3)	2.075
Ru2-O1	1.944(3)	1.980
Ru2-O2	1.940(3)	1.984
Ru2-O4	2.028(3)	2.095
Ru2-O5	2.072(3)	2.128
Ru2-O13	2.000(3)	2.055
Ru2-O14	2.007(3)	2.056
Ru3-O1	1.950(3)	1.986
Ru3-O2	1.934(3)	1.977
Ru3-O6	2.060(3)	2.137
Ru3-O7	2.048(3)	2.096
Ru3-O15	2.000(3)	2.053
Ru3-O16	2.029(4)	2.061
Ru4-O2	1.907(3)	1.906
Ru4-O8	2.066(4)	2.111
Ru4-O17	1.993(4)	2.044
Ru4-O18	1.992(4)	2.059
Ru4-O19	1.999(3)	2.055
Ru4-O20	2.029(4)	2.076
C31-O3	1.258(6)	1.263
C31-O4	1.265(6)	1.274
C33-O5	1.265(6)	1.270
C33-O6	1.260(6)	1.269
C35-O7	1.263(6)	1.274
C35-O8	1.256(7)	1.264
Ru2-Ru3	2.5187(6)	2.577
Ru1---Ru2	3.507	3.544
Ru1---Ru3	3.705	3.737
Ru1---Ru4	6.743	6.805
Ru2---Ru4	3.688	3.735
Ru3---Ru4	3.507	3.538

Table S3 Selected experimental and DFT calculated bond angles (deg) for **1**

1		
X-ray		DFT
O9-Ru1-O10	94.87(13)	94.46
O9-Ru1-O11	88.03(13)	87.07
O9-Ru1-O12	178.55(13)	177.15
O10-Ru1-O11	89.19(13)	88.33
O10-Ru1-O12	84.67(13)	87.32
O11-Ru1-O12	90.59(13)	90.77
O13-Ru2-O14	93.45(14)	92.21
O15-Ru3-O16	93.45(14)	92.26
O17-Ru4-O18	94.61(16)	94.10
O17-Ru4-O19	86.04(15)	87.56
O17-Ru4-O20	176.88(14)	176.89
O18-Ru4-O19	90.43(14)	89.52
O18-Ru4-O20	86.31(15)	86.75
O19-Ru4-O20	90.97(15)	90.64
Ru1-O1-Ru2	131.24(17)	131.46
Ru1-O1-Ru3	147.83(18)	147.46
Ru2-O2-Ru4	147.02(19)	147.49
Ru3-O2-Ru4	131.84(17)	131.31
Ru2-O1-Ru3	80.61(11)	81.055
Ru2-O2-Ru3	81.11(12)	81.17
Ru2-O2-Ru4	147.02(19)	147.49
Ru3-O2-Ru4	131.84(17)	131.31

Table S4 Energy calculations ((U)/(R)B3LYP /LanL2DZ/6-31G*)

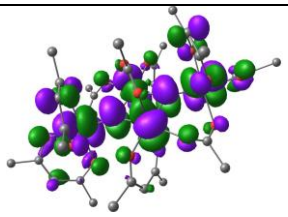
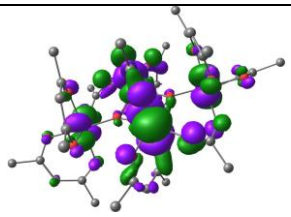
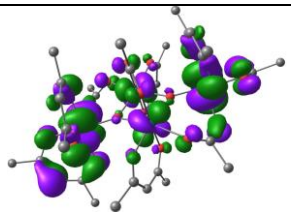
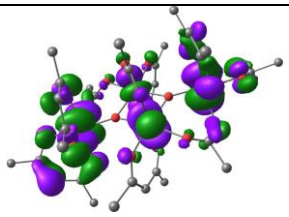
complex	*E* (Hartrees)						$\Delta E_{(HE\text{-}LE)}$ [a]
	S = 1/2	*S* = 3/2	*S* = 0	BS(1,1)*S* = 0[b]	*S* = 1	BS(1,1)*S* = 1	
1	-3283.02898	-3283.02099	-	-	-	-	0.00799 Hartrees 1453.6023 cm^{-1}
$\mathbf{1}^{+}$	-	-	-3282.8111	-3282.8171	-3282.8158	-3282.8138	0.00326 Hartrees 715.48729 cm^{-1}
$\mathbf{1}^{-}$	-	-	-3283.0976	-3283.1262	-3283.1260	-3283.1164	0.0098 Hartrees 2150.8510 cm^{-1}

[a]HE = Spin state in higher in energy and LE = Spin state in lower in energy

[b]Spin up and spin down electrons at the two interacting fragments

Table S5 DFT calculated selected MO compositions for **1** in *S* = 1/2 state (UB3LYP/ LanL2DZ/6-31G*)

MO	energy (eV)	% composition			
		Ru	acac	oxido	acetate
		α-MO			
LUMO+5	-0.584	12	85	01	02
LUMO+4	-0.605	09	89	00	02
LUMO+3	-0.636	15	82	02	01
LUMO+2	-0.684	06	93	01	01
LUMO+1	-2.253	74	08	15	03
LUMO	-3.065	65	08	24	03
SOMO	-4.773	57	21	17	06
HOMO-1	-4.976	68	19	03	09
HOMO-2	-5.201	65	28	01	07
HOMO-3	-5.252	60	34	02	04
HOMO-4	-5.323	64	29	00	07
HOMO-5	-5.417	58	36	01	05
		β-MO			
LUMO+5	-0.587	11	85	01	03
LUMO+4	-0.610	18	77	02	03
LUMO+3	-0.691	05	93	01	01
LUMO+2	-2.244	70	16	13	01
LUMO+1	-2.322	71	17	11	02
LUMO	-2.386	73	08	16	03
HOMO	-4.986	64	30	02	04
HOMO-1	-5.026	66	28	01	05
HOMO-2	-5.102	70	21	01	08
HOMO-3	-5.194	70	16	05	09
HOMO-4	-5.318	67	25	04	05
HOMO-5	-5.417	76	16	05	03

α-MO			
			
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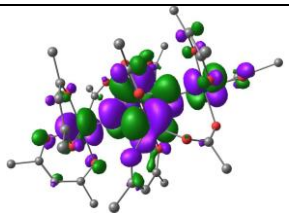
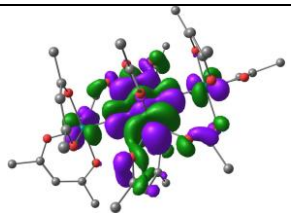
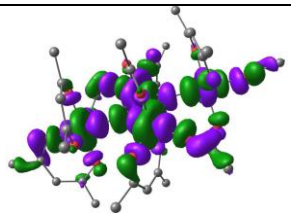
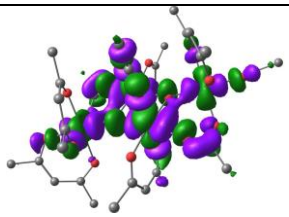
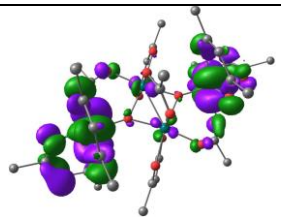
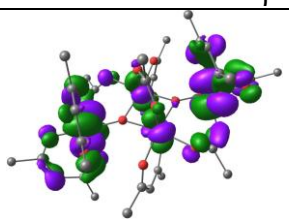
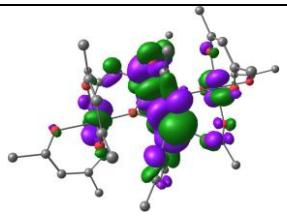
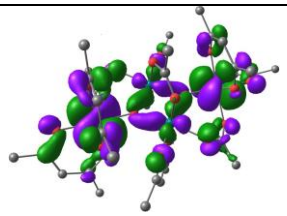
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
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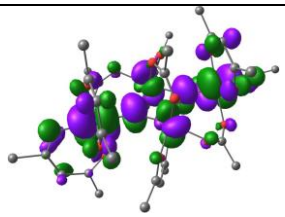
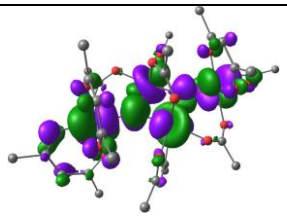
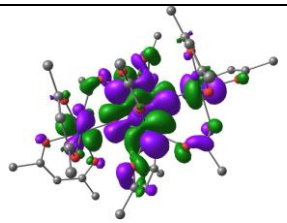
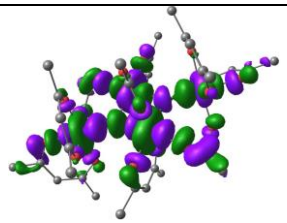
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S6 DFT calculated selected MO compositions for **1**$^{+}$ in *S* = 0 state (RB3LYP/LanL2DZ/6-31G*)

MO	energy (eV)	% composition			
		Ru	acac	oxido	acetate
LUMO+5	-3.660	11	86	01	02
LUMO+4	-3.876	58	25	06	11
LUMO+3	-4.106	58	29	02	11
LUMO+2	-4.208	62	21	07	10
LUMO+1	-5.605	75	07	15	03
LUMO	-6.477	63	18	17	02
HOMO	-7.984	56	30	10	04
HOMO-1	-8.117	40	51	01	08
HOMO-2	-8.301	56	35	04	05
HOMO-3	-8.431	52	37	07	04
HOMO-4	-8.530	32	57	02	08
HOMO-5	-8.584	36	59	02	03

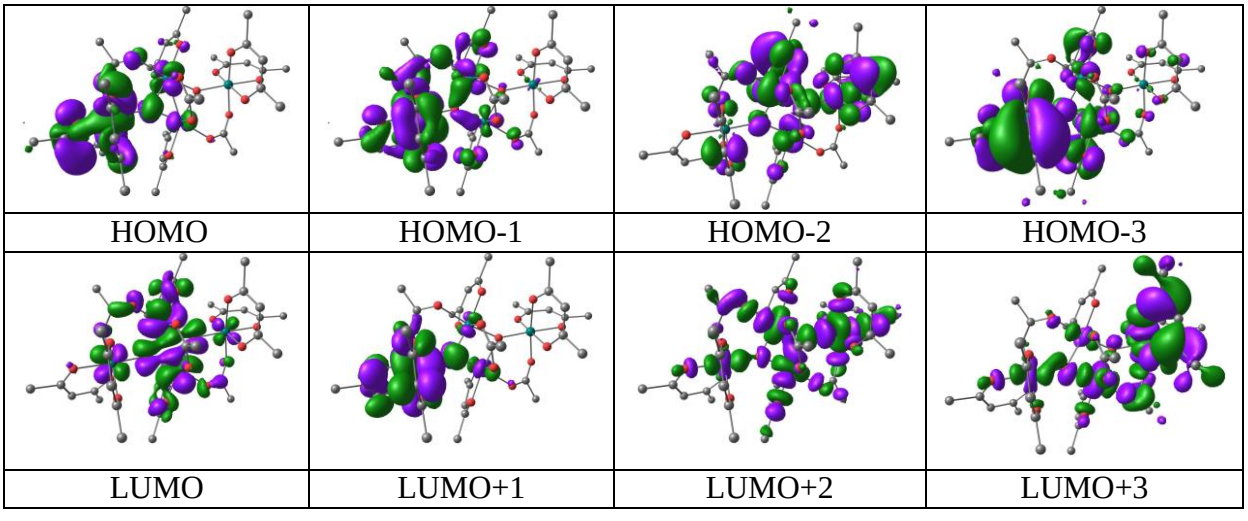
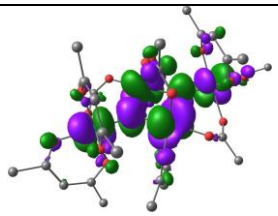
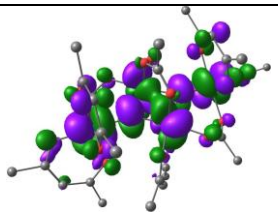
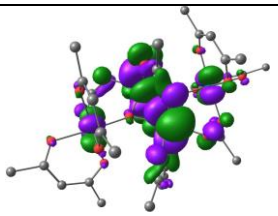
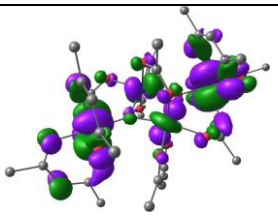


Table S7 DFT calculated selected MO compositions for **1**$^{-}$ in *S* = 0 state (RB3LYP/LanL2DZ/6-31G*)

MO	energy (eV)	% composition			
		Ru	acac	oxido	acetate
LUMO+5	1.925	04	95	00	00
LUMO+4	1.839	15	84	00	01
LUMO+3	1.804	18	81	00	01
LUMO+2	1.680	07	92	00	00
LUMO+1	1.666	07	92	00	01
LUMO	0.613	73	10	14	03
HOMO	-1.719	66	09	23	02
HOMO-1	-2.141	60	18	17	05
HOMO-2	-2.308	82	10	00	08
HOMO-3	-2.446	67	22	01	10
HOMO-4	-2.525	70	22	04	04
HOMO-5	-2.551	68	27	01	04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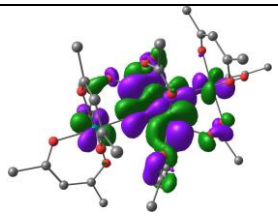	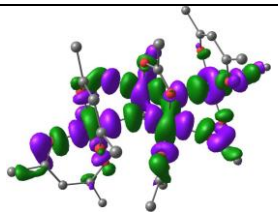	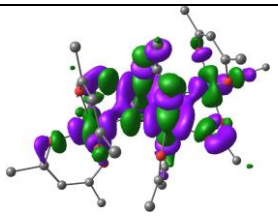	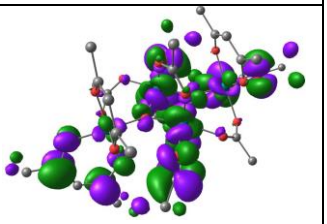
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S8 Electronic spectral data in CH_3CN

complex	λ/ nm (ε /dm^{3}cm^{-1} mol^{-1})
1$^+$	272(8800), 335(5300), 601(2400), 775(3600), 1156(890)
1	274(19600), 355(9600), 598(8000), 1350(880)
1$^-$	272(10500), 361(8800), 365(4500), 600(2800)