<Supporting Information>

Trinuclear ruthenium core-containing polyoxometalate-based hybrids: Preparation, Characterization and Catalysis Behavior

Huafeng Li, Peipei He, Rong Wan, Yan Zou, Xue Zhao, Pengtao Ma, Jingyang Niu* and Jingping Wang*

Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, China

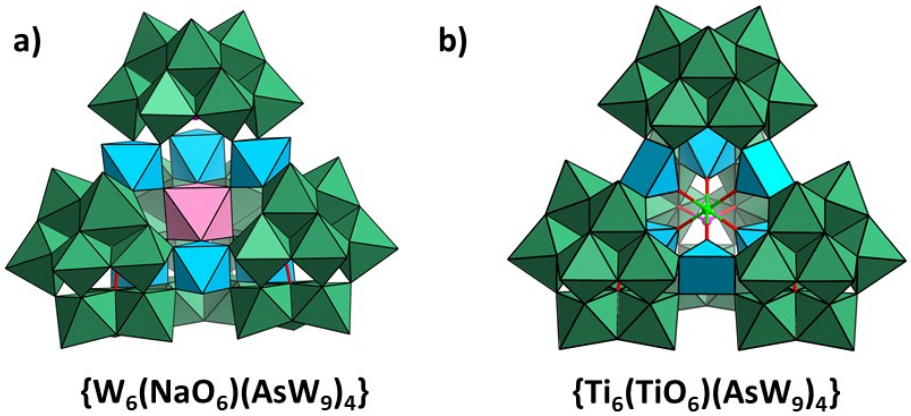

Figure S1. a) Combined polyhedral/ball-and-stick representation of polyanion for **1**. b) Combined polyhedral/ball-and-stick representation of polyanion for analogue. Color code: As (pink), Ti (bright green), NaO_6 octahedra (rose), WO_6 octahedra (sea green), bridging group WO_6 octahedron (sky blue) and TiO_5 pentahedron (blue); all hydrogen atoms have been omitted for clarity.

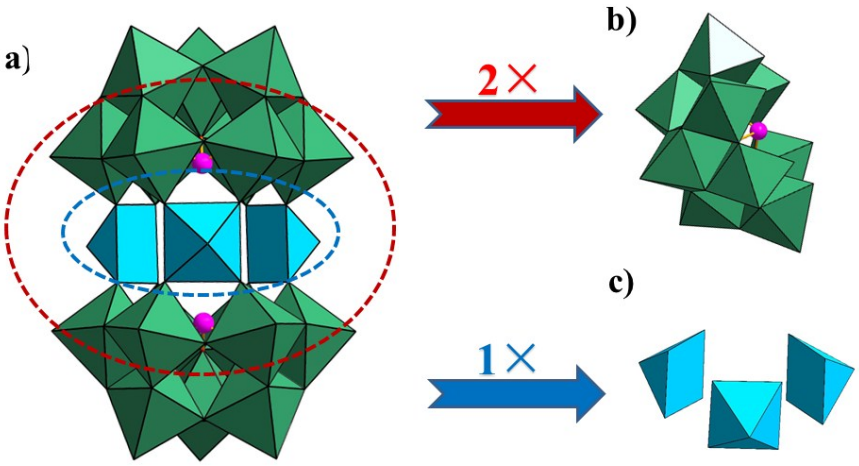

Figure S2. a) Combined polyhedral/ball-and-stick representation of polyanion for **2**. b) Polyhedral/ball-and-stick representation of $[\alpha\text{-}AsW_9O_{33}]^{9-}$ fragment. c) Polyhedral representation of three WO_5 fragments for **2**. Color code: As (pink), WO_6 octahedra (sea green) and bridging group WO_5 square-pyramidally (sky blue) ; all hydrogen atoms have been omitted for clarity.

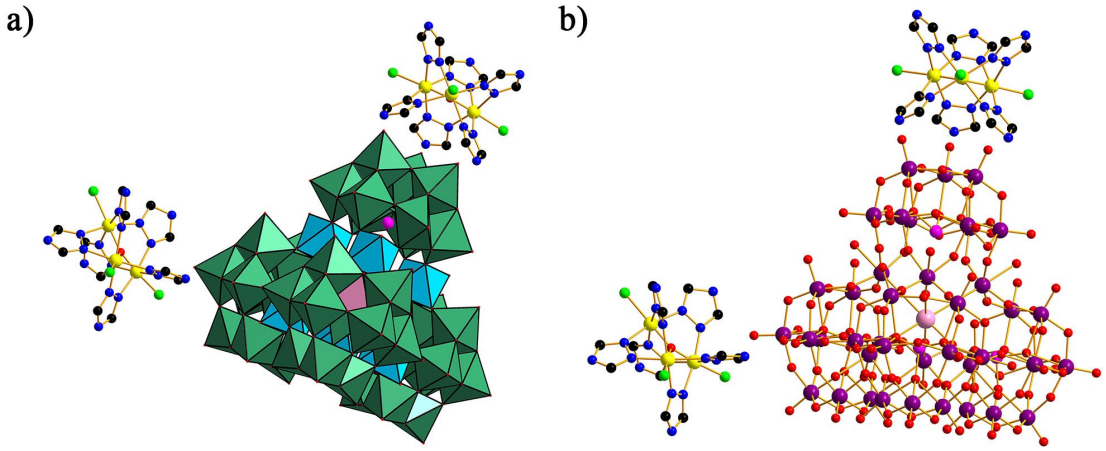

Figure S3. a) Polyhedral/ball-and-stick representation of compound **1**. b) Ball-and-stick representation of compound **1**. Color code: C (black), N (blue), O (red), Cl (bright green), Ru (yellow), As (pink), W (violet), Na (gray), NaO_6(rose), WO_6 octahedra (sea green) and bridging group WO_6 octahedron (sky blue); all hydrogen atoms have been omitted for clarity.

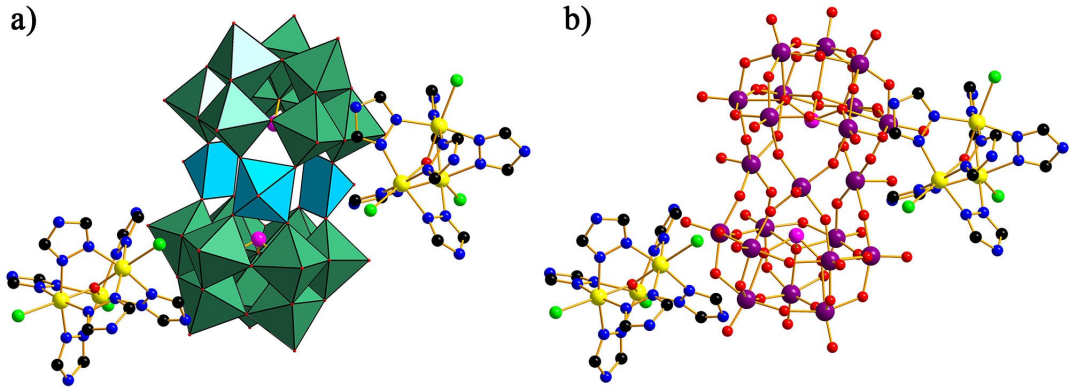

Figure S4. a) Polyhedral/ball-and-stick representation of compound **2**. b) Ball-and-stick representation of compound **2**. Color code: C (black), N (blue), O (red), Cl (bright green), Ru (yellow), As (pink), W (violet), WO_6 octahedra (sea green) and bridging group WO_5 square-pyramidally (sky blue); all hydrogen atoms have been omitted for clarity.

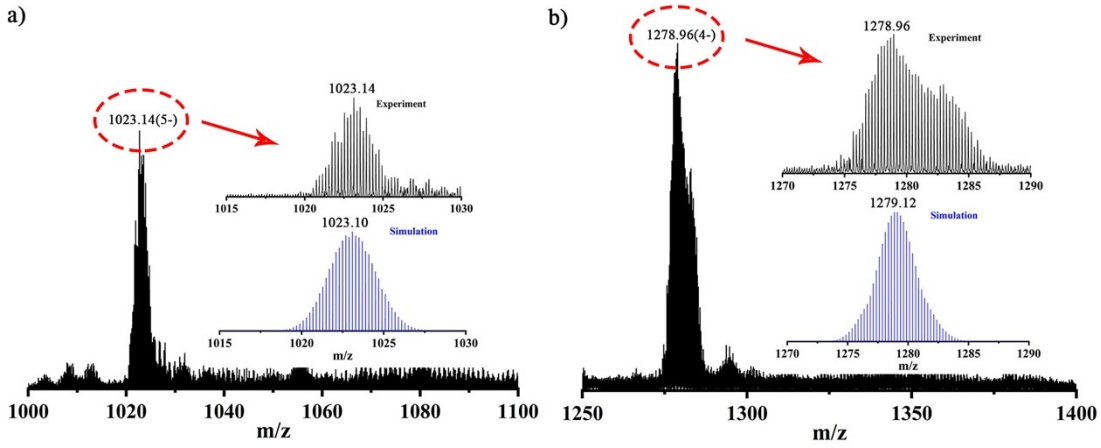

Figure S5. Negative mode ESI-MS of **2** and zoomed figure of peaks centered m/z 1023.14 and 1278.96, the simulated spectrum is shown in blue.

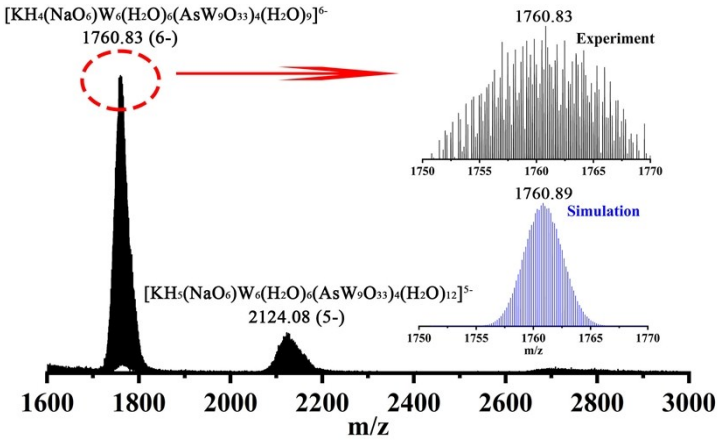

Figure S6. The ESI-MS spectrum of the catalyst **1** after five-run.

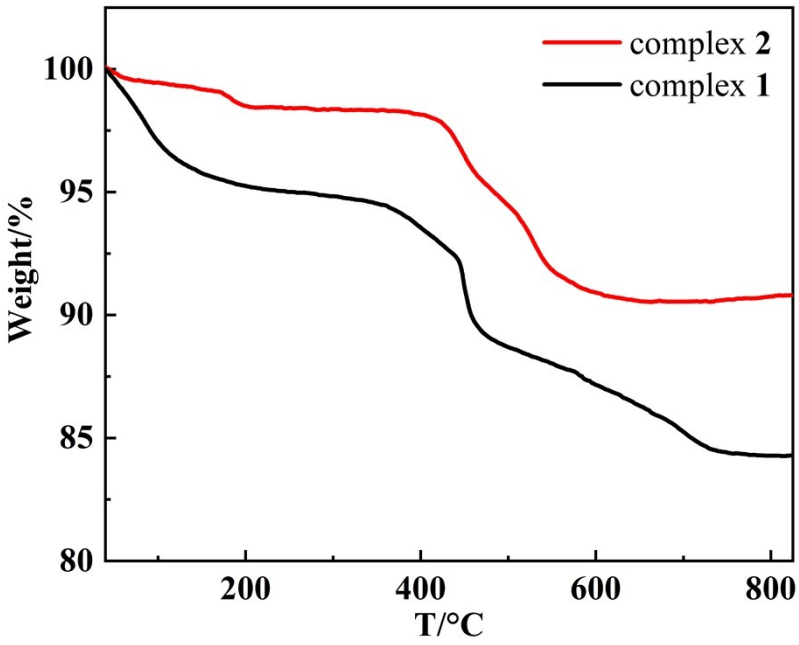

Figure S7. The thermogravimetric curves of **1** and **2**.

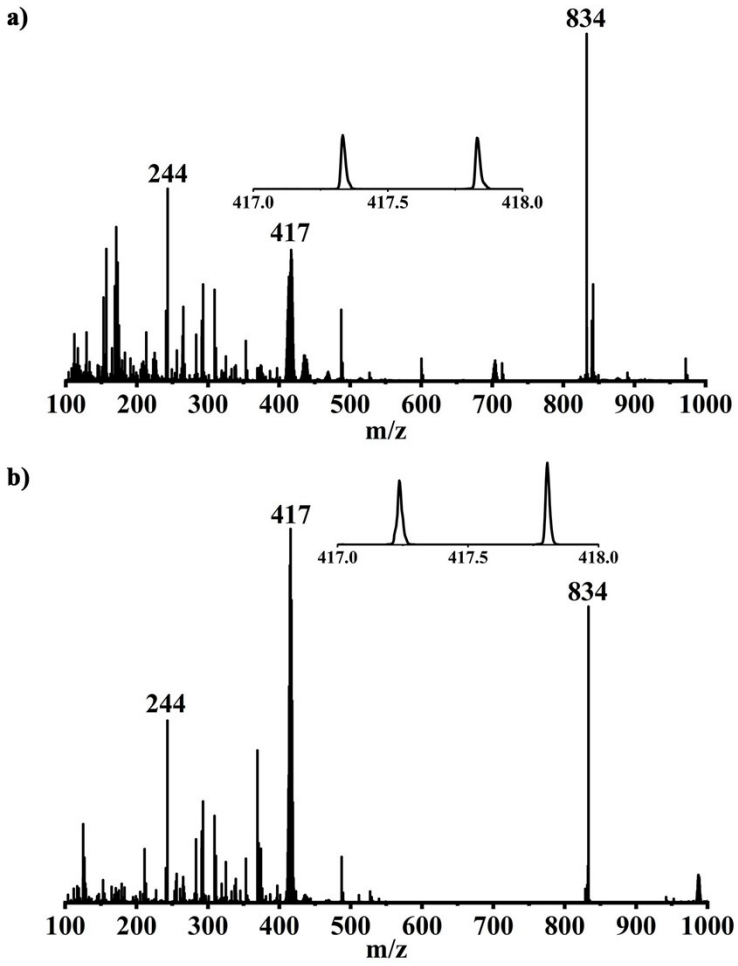

Figure S8 Positive mode ESI-MS of **1** and **2**.

Table S1. Selected bond distances of compounds **1** and **2**.

1		**2**	
Ru1–O146	1.88 (2)	Ru1–O34	1.855 (12)
Ru1–N1	2.01 (3)	Ru1–N1	2.04 (2)
Ru1–N10	2.07 (3)	Ru1–N5[2]	2.04 (2)
Ru1–N12	2.01 (3)	Ru1–N7	2.073 (19)
Ru1–N15	2.05 (3)	Ru1–N9	2.05 (2)
Ru1–Cl1	2.383 (9)	Ru1–Cl1	2.393 (8)
Ru2–O146	1.86 (2)	Ru2–O34	1.90 (2)
Ru2–N5	2.08 (3)	Ru2–N3[2]	2.081 (18)
Ru2–N7	2.08 (3)	Ru2–N3	2.081 (18)
Ru2–N14	2.05 (2)	Ru2–N4	2.090 (17)
Ru2–N36	1.95 (3)	Ru2–N4[2]	2.090 (17)
Ru2–Cl2	2.376 (10)	Ru2–Cl2	2.371 (13)
Ru3–O146	1.87 (2)	Ru3–O38	1.87 (2)
Ru3–N2	2.08 (3)	Ru3–N12	2.062 (19)
Ru3–N4	2.02 (3)	Ru3–N12[1]	2.062 (19)
Ru3–N6	2.06 (3)	Ru3–N14[1]	2.09 (2)
Ru3–N9	2.07 (2)	Ru3–N14	2.09 (2)
Ru3–Cl3	2.362 (10)	Ru3–Cl4	2.378 (12)

Table S2. Selected bond angles of compounds **1** and **2**.

1		**2**	
O146-Ru1-Cl1	178.5 (7)	O34-Ru1-Cl1	179.8 (6)
O146-Ru1-N1	84.7 (11)	O34-Ru1-N1	86.7 (9)
O146-Ru1-N10	85.0 (10)	O34-Ru1-N52	86.3 (9)
O146-Ru1-N12	85.1 (11)	O34-Ru1-N7	83.4 (8)
O146-Ru1-N15	83.2 (11)	O34-Ru1-N9	84.8 (10)
N1-Ru1-Cl1	95.6 (9)	N1-Ru1-Cl1	93.6 (7)
N1-Ru1-N10	81.6 (10)	N1-Ru1-N52	83.8 (8)
N1-Ru1-N12	169.5 (12)	N1-Ru1-N7	170.0 (8)
N1-Ru1-N15	94.9 (11)	N1-Ru1-N9	97.6 (8)
N10-Ru1-Cl1	93.5 (8)	N52-Ru1-Cl1	93.7 (6)
N12-Ru1- Cl1	94.5 (9)	N52-Ru1-N9	170.9 (9)
N12-Ru1-N10	95.2 (10)	N7-Ru1-Cl1	96.4 (6)
N12-Ru1- N15	86.2 (11)	N7-Ru1-N52	95.0 (8)
N15-Ru1-Cl1	98.3 (9)	N7-Ru1-N9	82.1 (8)
N15-Ru1-N10	168.0 (11)	N9-Ru1-Cl1	95.3 (7)
O146-Ru1-Cl1	178.5 (7)	O34-Ru1-Cl1	179.8 (6)
O146-Ru1-N1	84.7 (11)	O34-Ru1-N1	86.7 (9)
O146-Ru1-N10	85.0 (10)	O34-Ru1-N52	86.3 (9)

Table S3. BVS values of Ru, As, W and selected O atoms of compound **1**.

Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
Ru1	3.752	Ru2	3.802	Ru3	3.680	Ru4	3.570
Ru5	3.638	Ru6	3.858	As1	3.079	As2	2.940
As3	2.967	As4	2.971	W1	6.336	W2	6.150
W3	5.981	W4	6.080	W5	6.306	W6	5.981
W7	6.072	W8	6.242	W9	6.086	W10	6.232
W11	6.161	W12	6.314	W13	5.912	W14	5.857
W15	6.691	W16	6.012	W17	6.238	W18	6.196
W19	6.054	W20	5.880	W21	5.943	W22	6.412
W23	6.182	W24	6.066	W25	6.107	W26	6.263
W27	6.011	W28	6.356	W29	6.216	W30	6.242
W31	5.864	W32	6.260	W33	6.104	W34	6.594
W35	6.639	W36	5.827	W37	5.899	W38	6.004
W39	6.361	W40	6.326	W41	6.322	W42	5.944
O146	–2.290	O147	–2.322	O50	–0.213	O115	–0.264
O120	–0.278	O130	–0.243	O137	–0.310	O140	–0.286

Table S4. BVS values of Ru, As, W and selected O atoms of compound **2**.

Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
Ru1	3.696	Ru 2	3.810	Ru3	3.781	As1	3.076
W1	5.987	W2	6.170	W3	6.066	W4	6.257
W5	6.225	W6	6.018	W7	5.503	W8	6.121
W9	6.212	W10	6.423	W11	6.332	W12	6.010
O25	–2.058	O34	–2.293	O38	–2.273	O39	–0.832

Table S5. Crystal Data and Structure Refinements for compounds **1** and **2**.

Compound	**1**	**2**
Empirical Formula	$C_{24}H_{100}N_{36}Ru_6Cl_6KNaAs_4W_{42}O_{174}$	$C_{24}H_{40}N_{36}Ru_6Cl_6As_2W_{21}O_{77}$
Formula weight (g mol^{-1})	12579.38	6894.39
λ (Å)	0.71073	0.71073
T (K)	150(1)	150(1)
Crystal system	Triclinic	Monoclinic
Space group	*P-1*	$P2_1/m$
a (Å)	20.0498(11)	18.3691(5)
b (Å)	24.3323(11)	18.3890(6)
c (Å)	25.4119(12)	22.2929(6)
α (deg)	89.231(2)	90
β (deg)	72.661(2)	108.3577(12)
γ (deg)	80.351(2)	90
Volume (Å^3)	11657.8(10)	7147.1(4)
Z	2	2
D_{calc} (g cm^{-3})	3.474	3.195
μ (mm^{-1})	21.739	18.089
Limiting indices	–23≤h≤23	–21≤h≤21
	–29≤k≤29	–21≤k≤21,
	–30≤l≤29	–26≤l≤26
Reflns collected	171590	71079
R_{int}	0.0686	0.0789
Goodness-of-fit on F^2	1.134	1.025
R_1[a] *[I >2σ (I)]*	0.1042	0.0735
wR_2[b] *[I >2σ (I)]*	0.2754	0.1913
R_1[a] [all data]	0.1335	0.0983
wR_2[b] [all data]	0.3173	0.2175

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S6. The thermogravimetric analyses of compounds **1** and **2**.

Compound	Theoretical (two steps, %)	Experimental (two steps, %)
1	4.87, 10.48	4.96, 10.50
2	1.57, 7.77	1.62, 7.91

Thermogravimetric Analyses.

As shown in Figure S7, the thermal stability of compounds **1** and **2** have been determined by using thermogravimetric analyses. The thermogravimetric curves are very similar and show two major weight loss stages in the region of 50–825 ºC. Hence, only the thermogravimetric curve of **1** is taken as a representative to describe in detail. For **1**, the observed total weight loss (15.46 %) is agreement with the calculated value (15.35 %). The first weight loss of 4.96 % from 50 to 300 ºC was due to the release of twenty-eight lattice water molecules and six coordinated water ligands (calcd 4.87 %). The last weight loss of 10.50 % from 300 to 825 ºC was corresponded to the removal of two As_2O_3 molecules and twelve ligands (calcd 10.48 %). The first weight loss is more than the theoretical value, which may be ascribed to the fact that the samples have been weathered before the thermogravimetric analyses. The similar process of thermogravimetric analyses of compound **2** is shown in Table S6.