Electronic Supporting Information (ESI)

A step by step structural transformation of Ru-Ru bonding unit from paddle-wheel to edge-sharing bi-octahedra configuration

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Table S1-1. Crystal data and structural refinement parameters for compounds **1** and **2**

	Compound **1**	Compound **2**
Empirical formula	$C_{13}H_{20}F_6O_{10}Ru_2$	$C_{16}H_{14}F_{12}O_{10}Ru_2$
Formula weight	652.43	796.41
Temperature (K)	180(2)	150(2)
Wavelength (Å)	0.71073	1.34139
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*m*	$P2_1/c$
a /Å	14.9664(5)	14.2457(9)
b /Å	12.5079(4)	9.0514(5)
c /Å	12.8946(6)	18.7279(11)
β/°	112.313(2)	94.729(5)
V/Å^3	2233.11(15)	2406.6(2)
Z	4	4
ρ_{calc} (g ·cm^{-3})	1.941	2.198
μ (mm^{-1})	1.447	7.779
F (000)	1280	1544
Reflections collected	8577	5022
Reflections unique	2370	4884
parameters	157	362
GOF on F^2	1.090	0.906
R_{int}	0.0992	0.0547
R_1, wR_2[a] [$I>2\sigma(I)$]	0.0457, 0.1054	0.0667, 0.1601
R_1, wR_2[a] (all data)	0.0967, 0.1294	0.0789, 0.1683
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [e/Å^3]	2.409, -1.424	1.910, -1.400

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

Table S1-2. Crystal data and structural refinement parameters for compounds **3-cis** and **3-trans**

	Compound **3-*cis***	Compound **3-*trans***
Empirical formula	$C_{28}H_{26}Cl_2F_6O_{10}Ru_2$	$C_{28}H_{26}Cl_2F_6O_{10}Ru_2$
Formula weight	909.53	909.53
Temperature (K)	150(2)	150(2)
Wavelength (Å)	1.34139	1.34139
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a /Å	9.6208(4)	8.2762(5)
b /Å	11.5287(5)	10.0303(6)
c /Å	15.1896(6)	10.1906(6)
α /°	88.524(2)	75.829(3)
β /°	84.275(2)	79.539(3)
γ /°	80.366(2)	74.383(3)
V /Å^3	1652.64(12)	783.84(8)
Z	2	1
ρ_{calc} (g ·cm^{-3})	1.828	1.927
μ (mm^{-1})	6.525	6.878
F (000)	900	450
Reflections collected	36808	15488
Reflections unique	6714	3208
parameters	454	217
GOF on F^2	1.037	1.109
R_{int}	0.0522	0.0575
R_1, $wR_2{}^a$ [$I>2\sigma(I)$]	0.0368, 0.0776	0.0544, 0.1289
R_1, $wR_2{}^a$ (all data)	0.0559, 0.0851	0.0748, 0.1401
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [e/Å^3]	1.167, -0.825	1.902, -1.100

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

Table S1-3. Crystal data and structural refinement parameters for compounds **4-cis** and **4-trans**

	Compound **4-*cis***	Compound **4-*trans***
Empirical formula	$C_{18}H_{24}F_6O_{10}Ru_2$	$C_{18}H_{24}F_6O_{10}Ru_2$
Formula weight	716.51	716.51
Temperature (K)	150(2)	150(2)
Wavelength (Å)	1.34139	1.34139
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a /Å	7.9104(7)	8.408(19)
b /Å	17.5278(15)	17.66(4)
c /Å	17.9103(17)	8.367(19)
α /°	90	90
β /°	90.068(5)	99.14(10)
γ /°	90	90

V/Å^3	2483.3(4)	1227(5)
Z	4	2
ρ_{calc} (g ·cm^{-3})	1.916	1.940
μ (mm^{-1})	7.252	7.340
F (000)	1416	708
Reflections collected	33008	11801
Reflections unique	5040	2311
parameters	352	191
GOF on F^2	1.041	1.014
R_{int}	0.1312	0.1381
R_1, $wR_2{}^a$ [$I>2\sigma(I)$]	0.0529, 0.1105	0.0817, 0.1943
R_1, $wR_2{}^a$ (all data)	0.1154, 0.1308	0.1060, 0.2071
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [e/Å^3]	1.160, -1.323	1.704, -1.582

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

Table S2. Selected bond distances (Å) and angles (˚) for compound **1**

Selected bond distances (Å)			
Ru(1)-Ru(2)	2.4682(11)	C(9)-F(1)	1.327(9)
Ru(1)-O(1)	2.001(5)	C(9)-F(2)	1.342(10)
Ru(1)-O(2)	2.076(6)	C(9)-F(3)	1.320(9)
Ru(1)-O(4)	2.074(7)	C(6)-O(1)	1.445(9)
Ru(1)-O(6)	1.992(5)	C(1)-O(2)	1.269(11)
Ru(1)-O(1A)	2.001(5)	C(1)-O(3)	1.279(13)
Ru(1)-O(6A)	1.992(5)	C(3)-O(4)	1.283(14)
Ru(2)-O(1)	1.994(5)	C(3)-O(5)	1.279(12)
Ru(2)-O(3)	2.070(6)	C(5)-O(6)	1.416(9)
Ru(2)-O(5)	2.056(6)	C(7)-O(7)	1.269(9)
Ru(2)-O(7)	2.025(5)	C(1)-C(2)	1.497(15)
Ru(2)-O(1^i)	1.994(5)	C(3)-C(4)	1.497(16)
Ru(2)-O(7^i)	2.025(5)	C(7)-C(8)	1.383(9)
		C(7)-C(9)	1.519(11)
Selected angles (˚)			
Ru(1)-O(1)-Ru(2)	76.31(18)		
Ru(2)-Ru(1)-O(1)	51.71(13)	Ru(1)-Ru(2)-O(1)	51.98(13)
Ru(2)-Ru(1)-O(2)	87.38(18)	Ru(1)-Ru(2)-O(3)	87.15(18)
Ru(2)-Ru(1)-O(4)	86.7(2)	Ru(1)-Ru(2)-O(5)	88.16(18)
Ru(2)-Ru(1)-O(6)	136.04(14)	Ru(1)-Ru(2)-O(7)	134.89(14)
Ru(2)-Ru(1)-O(1^i)	51.71(13)	Ru(1)-Ru(2)-O(1^i)	51.98(13)
Ru(2)-Ru(1)-O(6^i)	136.04(14)	Ru(1)-Ru(2)-O(7^i)	134.89(14)
O(1)-Ru(1)-O(2)	92.72(16)	O(1)-Ru(2)-O(3)	92.60(16)
O(1)-Ru(1)-O(4)	83.59(17)	O(1)-Ru(2)-O(5)	84.50(16)
O(1)-Ru(1)-O(6)	84.98(19)	O(1)-Ru(2)-O(7)	83.19(19)
O(1)-Ru(1)-O(1^i)	102.74(19)	O(1)-Ru(2)-O(1^i)	103.28(19)
O(1)-Ru(1)-O(6^i)	172.2(2)	O(1)-Ru(2)-O(7^i)	172.7(2)

O(2)-Ru(1)-O(4)	174.1(3)	O(3)-Ru(2)-O(5)	175.3(2)
O(2)-Ru(1)-O(6)	87.70(19)	O(3)-Ru(2)-O(7)	90.55(18)
O(1A)-Ru(1)-O(2)	92.72(16)	O(1A)-Ru(2)-O(3)	92.60(16)
O(2)-Ru(1)-O(6^{i})	87.70(19)	O(3)-Ru(2)-O(7^{i})	90.55(18)
O(4)-Ru(1)-O(6)	96.6(2)	O(5)-Ru(2)-O(7)	92.76(19)
O(1A)-Ru(1)-O(4)	83.59(17)	O(1A)-Ru(2)-O(5)	84.50(16)
O(4)-Ru(1)-O(6^{i})	96.6(2)	O(5)-Ru(2)-O(7^{i})	92.76(19)
O(1A)-Ru(1)-O(6)	172.2(2)	O(1A)-Ru(2)-O(7)	172.7(2)
O(6)-Ru(1)-O(6^{i})	87.3(2)	O(7)-Ru(2)-O(7^{i})	90.1(2)
O(1A)-Ru(1)-O(6^{i})	84.98(19)	O(1A)-Ru(2)-O(7^{i})	83.19(19)
Ru(1)-O(1)-C(6)	120.9(4)	Ru(2)-O(1)-C(6)	122.5(4)
Ru(1)-O(2)-C(1)	119.6(6)	Ru(2)-O(3)-C(1)	119.9(6)
Ru(1)-O(4)-C(3)	119.9(6)	Ru(2)-O(5)-C(3)	119.3(6)
Ru(1)-O(6)-C(5)	122.8(4)	Ru(2)-O(7)-C(7)	123.8(5)
O(2)-C(1)-O(3)	126.0(9)	O(3)-C(1)-C(2)	116.7(8)
O(2)-C(1)-C(2)	117.3(9)	O(4)-C(3)-C(4)	117.3(9)
O(5)-C(3)-C(4)	116.7(10)	O(4)-C(3)-O(5)	126.0(10)
C(8)-C(7)-C(9)	117.5(7)	C(7-C(8-C(7^{i})	121.4(8)
O(7)-C(7)-C(8)	129.5(7)	O(7)-C(7)-C(9)	113.0(6)
F(1)-C(9)-F(3)	106.9(6)	F(1)-C(9)-C(7)	113.8(6)
F(2)-C(9)-C(7)	110.0(6)	F(2)-C(9)-F(3)	107.0(6)
F(1)-C(9)-F(2)	105.1(6)	F(3)-C(9)-C(7)	113.5(6)

Symmetry transformations used to generate equivalent atoms: i, x, -y, z

Table S3. Selected bond distances (Å) and angles (˚) for compound **2**

Selected bond distances (Å)			
Ru(1)-Ru(1^{i})	2.4584(11)	Ru(2)-Ru(2B)	2.4526(13)
Ru(1)-O(1)	1.980(6)	Ru(2)-O(6)	1.986(8)
Ru(1)-O(2)	2.070(8)	Ru(2)-O(7)	2.045(7)
Ru(1)-O(4)	2.033(7)	Ru(2)-O(9)	2.017(8)
Ru(1)-O(5)	2.012(7)	Ru(2)-O(10)	2.034(7)
Ru(1)-O(1A)	1.983(7)	Ru(2)-O(6B)	1.974(8)
Ru(1)-O(3A)	2.061(7)	Ru(2)-O(8B)	2.082(7)
O(1)-C(1)	1.432(13)	C(2)-C(3)	1.482(16)
O(2)-C(2)	1.298(14)	C(4)-C(5)	1.525(15)
O(3)-C(2)	1.262(12)	C(5)-C(6)	1.382(15)
O(4)-C(5)	1.261(12)	C(6)-C(7)	1.378(16)
O(5)-C(7)	1.275(12)	C(7)-C(8)	1.532(16)
O(6)-C(9)	1.469(14)	C(10)-C(11)	1.501(17)
O(7)-C(10)	1.263(15)	C(12)-C(13)	1.508(16)
O(8)-C(10)	1.276(14)	C(13)-C(14)	1.393(17)
O(9)-C(13)	1.268(14)	C(14)-C(15)	1.382(16)
O(10)-C(15)	1.263(14)	C(15)-C(16)	1.534(16)
F(1)-C(4)	1.303(16)	F(7)-C(12)	1.327(14)

F(2)-C(4)	1.308(17)	F(8)-C(12)	1.332(14)
F(3)-C(4)	1.301(14)	F(9)-C(12)	1.317(14)
F(4)-C(8)	1.329(17)	F(10)-C(16)	1.312(16)
F(5)-C(8)	1.278(13)	F(11)-C(16)	1.303(15)
F(6)-C(8)	1.285(16)	F(12)-C(16)	1.296(17)
Selected angles (˚)			
Ru(1)-O(1)-Ru(1A)	76.7(2)	Ru(2)-O(6)-Ru(2B)	76.5(3)
Ru(1A)-Ru(1)-O(1)	51.7(2)	Ru(2B)-Ru(2)-O(6)	51.5(2)
Ru(1A)-Ru(1)-O(2)	87.1(2)	Ru(2B)-Ru(2)-O(7)	88.3(2)
Ru(1A)-Ru(1)-O(4)	136.0(2)	Ru(2B)-Ru(2)-O(9)	134.7(2)
Ru(1A)-Ru(1)-O(5)	134.7(2)	Ru(2B)-Ru(2)-O(8B)	86.7(2)
Ru(1A)-Ru(1)-O(1A)	51.6(2)	Ru(2B)-Ru(2)-O(10)	134.6(2)
Ru(1A)-Ru(1)-O(3A)	87.7(2)	Ru(2B)-Ru(2)-O(6B)	51.9(2)
O(1)-Ru(1)-O(2)	84.0(3)	O(6B)-Ru(2)-O(8B)	82.9(3)
O(1)-Ru(1)-O(4)	84.5(3)	O(6)-Ru(2)-O(6B)	103.5(3)
O(1)-Ru(1)-O(5)	172.5(3)	O(6)-Ru(2)-O(8B)	93.0(3)
O(1)-Ru(1)-O(1^{i})	103.3(3)	O(7)-Ru(2)-O(9)	88.8(3)
O(1)-Ru(1)-O(3^{i})	93.2(3)	O(7)-Ru(2)-O(10)	90.0(3)
O(2)-Ru(1)-O(4)	93.5(3)	O(6B)-Ru(2)-O(7)	94.0(3)
O(2)-Ru(1)-O(5)	92.3(3)	O(7)-Ru(2)-O(8B)	175.0(3)
O(1A)-Ru(1)-O(2)	92.4(3)	O(9)-Ru(2)-O(10)	90.7(3)
O(2)-Ru(1)-O(3A)	174.8(3)	O(6B)-Ru(2)-O(9)	173.0(3)
O(4)-Ru(1)-O(5)	89.3(3)	O(8B)-Ru(2)-O(9)	94.7(3)
O(1A)-Ru(1)-O(4)	136.0(2)	O(6)-Ru(2)-O(7)	83.9(3)
O(3A)-Ru(1)-O(4)	90.6(3)	O(6)-Ru(2)-O(9)	83.2(3)
O(1A)-Ru(1)-O(5)	83.3(3)	O(6)-Ru(2)-O(10)	171.4(3)
O(3A)-Ru(1)-O(5)	91.0(3)	O(6B)-Ru(2)-O(10)	82.9(3)
O(1A)-Ru(1)-O(3A)	83.9(3)	O(8B)-Ru(2)-O(10)	93.5(3)
Ru(1)-O(1)-C(1)	123.7(7)	Ru(2)-O(6)-C(9)	121.6(7)
Ru(1A)-O(1)-C(1)	122.6(6)	Ru(2B)-O(6)-C(9)	121.6(6)
Ru(1)-O(2)-C(8)	126.0(9)	Ru(2)-O(7)-C(10)	119.1(7)
Ru(1)-O(5)-C(10)	125.7(9)	Ru(2B)-O(8)-C(10)	118.7(7)
Ru(1A)-O(3)-C(2)	120.4(7)	Ru(2)-O(9)-C(13)	125.6(7)
Ru(1)-O(2)-C(2)	119.7(7)	Ru(2)-O(10)-C(15)	123.0(7)
Ru(1)-O(4)-C(5)	125.1(7)	O(4)-C(5)-C(6)	129.0(10)
Ru(1)-O(5)-C(7)	125.9(7)	O(4)-C(5)-C(4)	112.9(9)
O(2)-C(2)-O(3)	125.0(10)	O(7)-C(10)-O(8)	126.8(10)
O(3)-C(2)-C(3)	117.2(10)	O(7)-C(10)-C(11)	117.6(10)
O(2)-C(2)-C(3)	117.9(9)	O(8)-C(10)-C(11)	115.6(11)
F(1)-C(4)-F(3)	107.4(11)	F(7)-C(12)-F(8)	107.0(10)
F(1)-C(4)-F(2)	104.6(10)	F(7)-C(12)-F(9)	107.4(10)
F(1)-C(4)-C(5)	113.3(11)	F(7)-C(12)-C(13)	111.9(10)
F(2)-C(4)-F(3)	106.5(12)	F(8)-C(12)-F(9)	107.2(9)
F(2)-C(4)-C(5)	110.8(10)	F(8)-C(12)-C(13)	110.2(10)

F(3)-C(4)-C(5)	113.6(9)	F(9)-C(12)-C(13)	112.9(10)
O(4)-C(5)-C(6)	129.0(10)	O(9)-C(13)-C(12)	115.5(10)
C(4)-C(5)-C(6)	118.1(9)	C(9)-C(13)-C(14)	127.1(11)
O(4)-C(8)-C(7)	113.6(12)	C(12)-C(13)-C(14)	117.3(10)
C(5)-C(6)-C(7)	122.1(10)	O(10)-C(15)-C(14)	129.9(11)
O(5)-C(7)-C(6)	128.3(10)	O(10)-C(15)-C(16)	111.3(10)
O(5)-C(7)-C(8)	112.2(9)	C(13)-C(14)-C(15)	123.1(11)
C(6)-C(7)-C(8)	119.3(9)	F(10)-C(16)-F(11)	106.3(10)
F(4)-C(8)-C(7)	109.5(10)	F(8)-C(12)-F(9)	106.8(13)
F(5)-C(8)-F(6)	108.5(11)	F(10)-C(16)-F(12)	107.7(12)
F(4)-C(8)-F(6)	105.1(10)	F(10)-C(16)-C(15)	113.2(10)
F(4)-C(8)-F(5)	107.4(12)	F(11)-C(16)-F(12)	106.8(11)
F(5)-C(8)-F(7)	113.8(9)	C(14)-C(15)-C(16)	118.9(10)
F(6)-C(8)-C(7)	112.1(11)		

Symmetry transformations used to generate equivalent atoms: A, 1-x, 1-y, 1-z; B, -x, 1-y, 1-z.

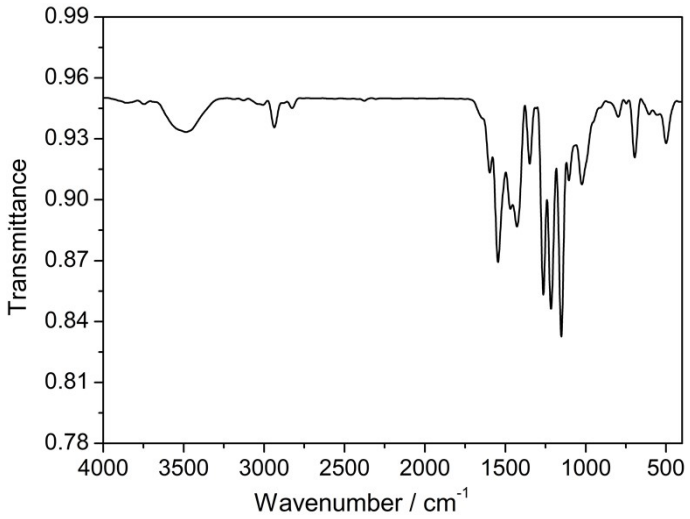

Fig. S1 IR spectrum of compound **1**.

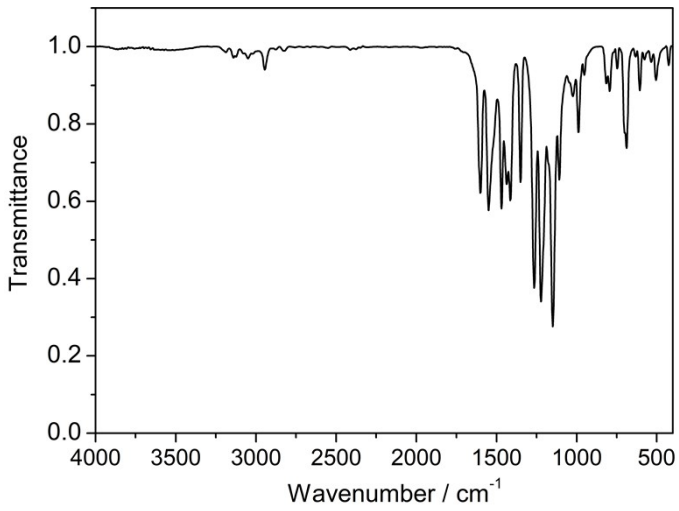

Fig. S2 IR spectrum of compound **2**.

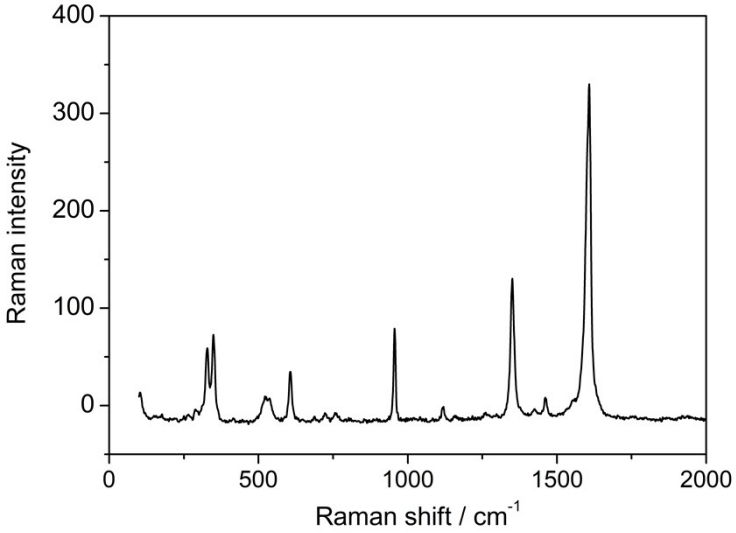

Fig. S3 Raman spectrum of compound **1**.

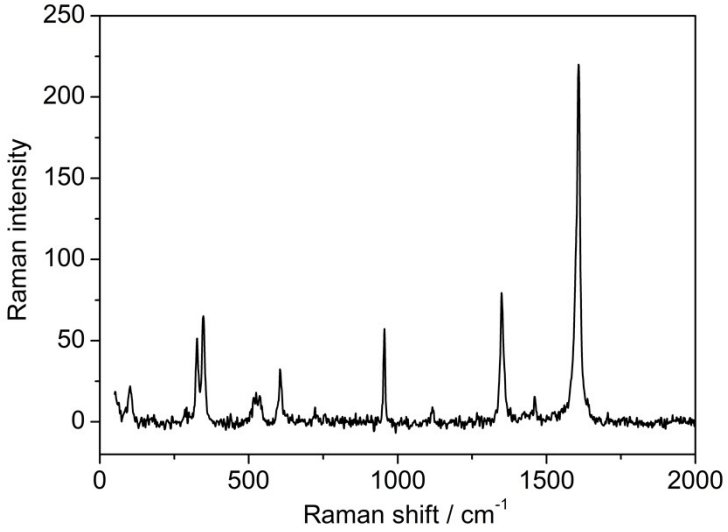

Fig. S4 Raman spectrum of compound **2**.

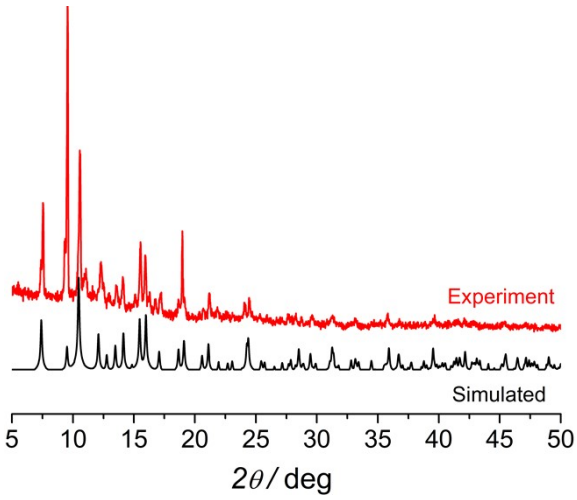

Fig. S5 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and the as-synthesized product of **1.**

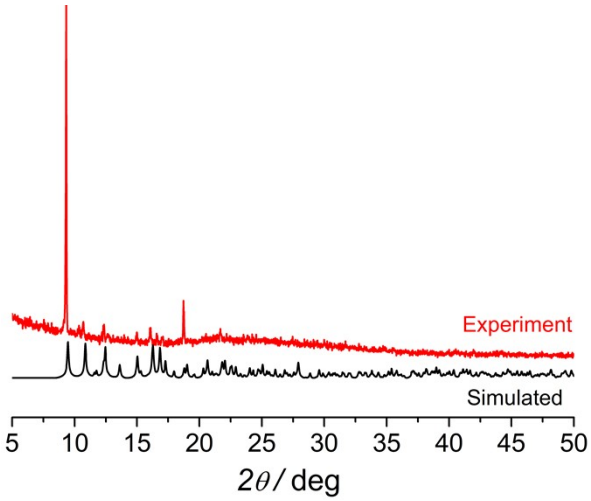

Fig. S6 Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and the as-synthesized product of **2.**

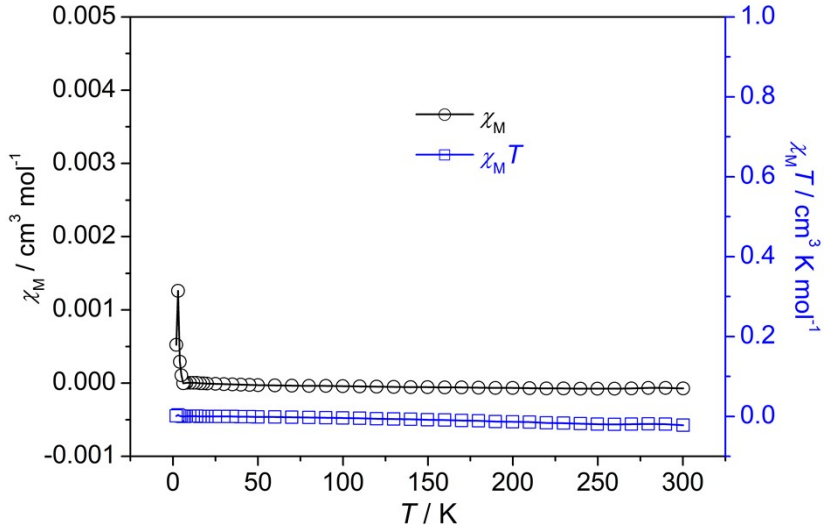

Fig. S7 χ_M and $\chi_M T$ vs. T plots of compound **1.**

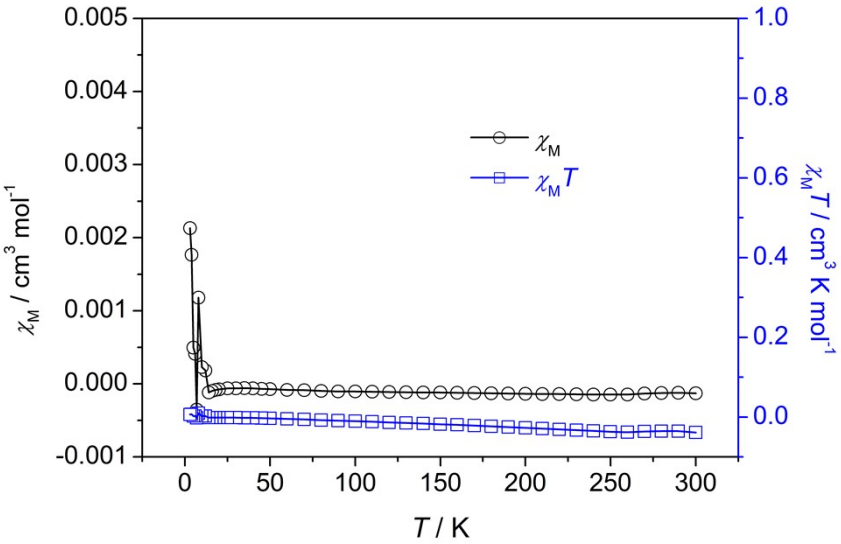

Fig. S8 χ_M and $\chi_M T$ vs. T plots of compound **2.**

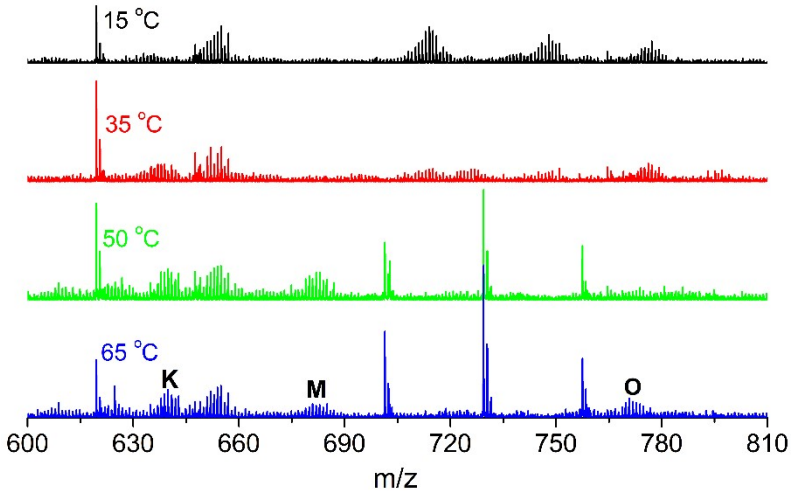

Fig. S9 Zoom in the positive mode electrospray mass spectra of $Ru_2(CH_3CO_2)_4Cl$ and $(CH_3CH_2)_3N$ dissolved in methanol solution.

Table S4 The formulae of the species detected in ESI-MS with positive mode of $Ru_2(OAc)_4Cl$ and Et_3N dissolved in CH_3OH.

Peaks	Fragments	Exp	Simu
A	$Ru_2(OAc)_4^+$	438.95	438.86
B	$Ru_2(OAc)_4(H_2O)^+$	456.87	456.87
C	$Ru_2(OAc)_3(CH_3O)(Et_3N)^+$	512.91	512.02
	$Ru_2(OAc)_3Cl(Et_3N)^+$	516.86	516.95
D	$Ru_2(OAc)_4Et_3NHCl^+$	575.86	575.90
K	$Ru_2(OAc)_2(CH_3O)_2(hfac)(CH_3OH)(H_2O)^+$	639.90	639.86
M	$Ru_2(OAc)_2(hfac)(CH_3O)(OH)(Et_3N)^+$	681.97	681.01
O	$Ru_2(OAc)_2(CH_3O)(hfac)_2^+$	770.23	769.90

Table S5 The formulae of the species detected in ESI-MS with negative mode of $Ru_2(OAc)_4Cl$ and Et_3N dissolved in CH_3OH.

Peaks	Fragments	Exp	Simu
a	$Ru_2(OAc)_2(hfac)^-$	528.70	528.28
b	$Ru_2(OAc)_2(CH_3O)(hfac)^-$	558.84	558.84
c	$[Ru_2(OAc)_2(CH_3O)_2(hfac)^-$	590.35	590.86
d	$Ru_2(OAc)_2(OCH_3)_2(hfac)(CH_3OH)^-$	622.19	622.39
e	$Ru_2(OAc)_2(OCH_3)_4(hfac)^-$	652.35	652.37
f	$Ru_2(OAc)_2(CH_3O)_2(hfac)(CH_3OH)_2N_2^-$	676.95	679.91
g	$Ru_2(OAc)_2(CH_3O)_4(hfac)(CH_3OH)^-$	688.48	688.49
i	$Ru_2(OAc)_2(CH_3O)_2(hfac)(CH_3OH)_3(H_2O)_2^-$	722.91	722.96
j	$Ru_2(OAc)_2(hfac)_2^-$	736.82	736.84
k	$Ru_2(OAc)_2(hfac)_2(OH)^-$	752.36	752.34
l	$Ru_2(OAc)_2(hfac)_2(CH_3OH)^-$	766.93	768.38
n	$Ru_2(OAc)_2(hfac)_2(N_2)(OH)^-$	782.36	782.54
o	$Ru_2(OAc)_2(CH_3O)_2(hfac)_2^-$	799.87	799.89

p	$Ru_2(OAc)_2(CH_3O)_2(hfac)_2(OH)^-$	814.54	814.37
q	$Ru_2(OAc)_2(CH_3O)_3(hfac)_2^-$	827.81	827.91
r	$Ru_2(OAc)_2(hfac)_2(Et_3N)(OH)^-$	856.92	856.54
s	$Ru_2(OAc)_2(hfac)_2(Et_3N)(N_2)(OH)^-$	882.95	882.55

Table S6 The formulae of the species detected in ESI-MS with positive mode of compound **1** dissolved in CH_3OH.

Peaks	Fragments	Exp	Simu
E	$Ru_2(OAc)_2(hfac)^+$	531.88	530.80
F	$Ru_2(OAc)_2(CH_3O)(hfac)^+$	561.86	561.87
G	$Ru_2(OAc)_2(CH_3O)(OH)(hfac)^+$	578.85	578.96
H	$Ru_2(OAc)_2(CH_3O)_2(hfac)^+$	591.50	590.80
I	$Ru_2(OAc)_2(CH_3O)_2(hfac)(H_2O)^+$	608.88	607.92
J	$Ru_2(OAc)_2(CH_3O)_2(hfac)(CH_3OH)^+$	619.58	623.95
K	$Ru_2(OAc)_2(CH_3O)_2(hfac)(CH_3OH)(H_2O)^+$	639.90	639.90
L	$Ru_2(OAc)_2(CH_3O)_2(hfac)(CH_3OH)_2^+$	654.91	654.92
N	$Ru_2(OAc)_2(hfac)_2^+$	739.83	739.99
O	$Ru_2(OAc)_2(CH_3O)(hfac)_2^+$	770.82	769.90
P	$Ru_2(OAc)_2(CH_3O)(hfac)_2(H_2O)^+$	788.95	788.89
Q	$Ru_2(OAc)_2(CH_3O)(hfac)_2(CH_3OH)^+$	802.96	801.92
R	$Ru_2(OAc)_2(CH_3O)(hfac)_2(CH_3OH)(H_2O)^+$	824.89	820.80
	$Ru_2(OAc)_2(CH_3O)(hfac)_2(CH_3OH)_2^+$	829.90	830.00
S	$Ru_2(OAc)_2(CH_3O)(hfac)_2(CH_3OH)_2(H_2O)^+$	851.93	851.90

Table S7 The formulae of the species detected in ESI-MS with negative mode of compound **1** dissolved in CH_3OH.

Peaks	Fragments	Exp	Simu
a	$Ru_2(OAc)_2(hfac)^-$	528.69	528.28
b	$Ru_2(OAc)_2(CH_3O)(hfac)^-$	558.84	558.84
c	$Ru_2(OAc)_2(CH_3O)_2(hfac)^-$	590.35	590.86
d	$Ru_2(OAc)_2(CH_3O)_3(hfac)^-$	622.19	622.39
e	$Ru_2(OAc)_2(CH_3O)_4(hfac)^-$	652.91	652.90
f	$Ru_2(OAc)_2(OCH_3)_4(hfac)N_2^-$	676.95	679.91
h	$Ru_2(OAc)(CH_3O)(hfac)_2^-$	706.82	707.32
j	$Ru_2(OAc)_2(hfac)_2^-$	736.82	736.84
l	$Ru_2(OAc)_2(CH_3O)(hfac)_2^-$	768.87	768.38
m	$Ru_2(OAc)_2(hfac)_2(OH)_2^-$	772.92	772.37
o	$Ru_2(OAc)_2(CH_3O)_2(hfac)_2^-$	799.87	799.89
q	$Ru_2(OAc)_2(CH_3O)_3(hfac)_2^-$	827.81	827.91

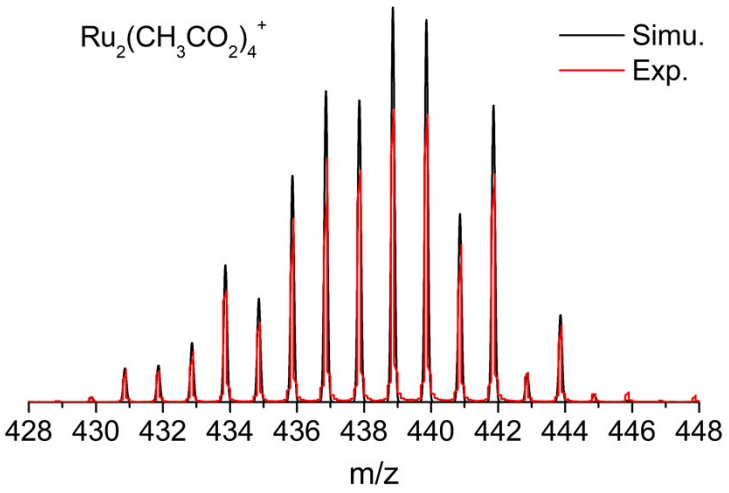

Fig. S10 The theoretical and experimental isotope distributions of species A.

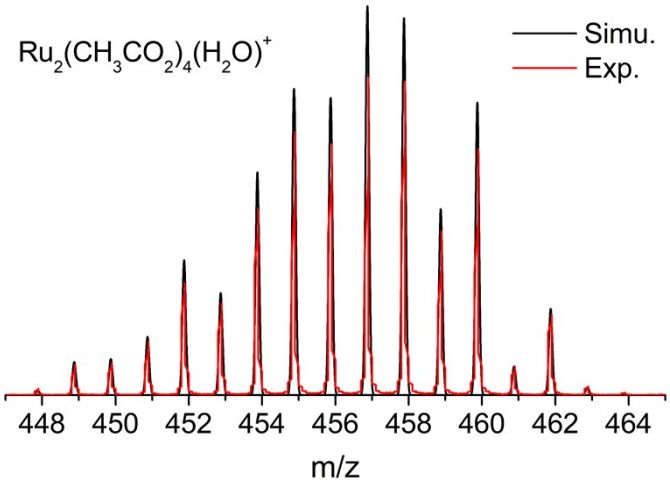

Fig. S11 The theoretical and experimental isotope distributions of species B $Ru_2(CH_3CO_2)_4(H_2O)^+$.

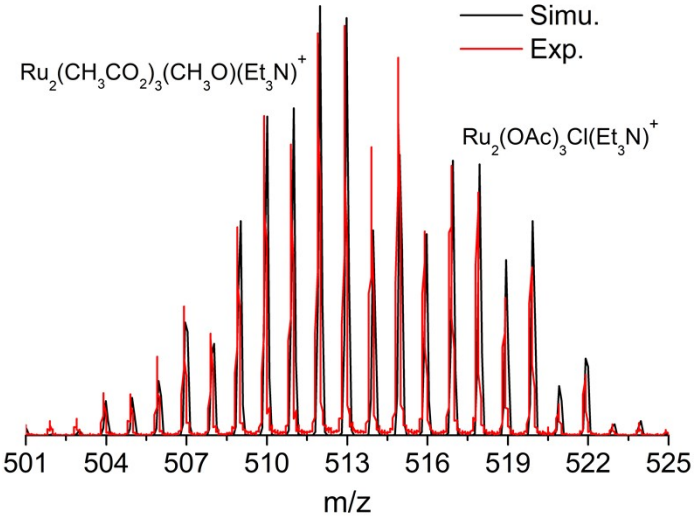

Fig. S12 The theoretical and experimental isotope distributions of species C $Ru_2(CH_3CO_2)_3(CH_3O)(Et_3N)^+$ and $Ru_2(CH_3CO_2)_3Cl(Et_3N)^+$

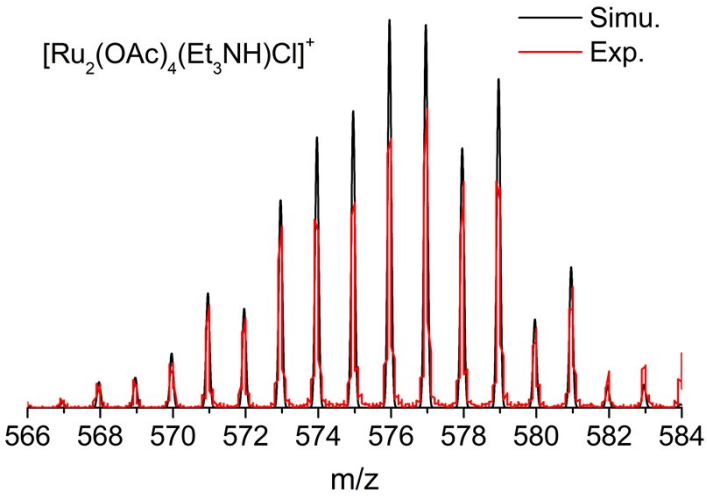

Fig. S13 The theoretical and experimental isotope distributions of species D .

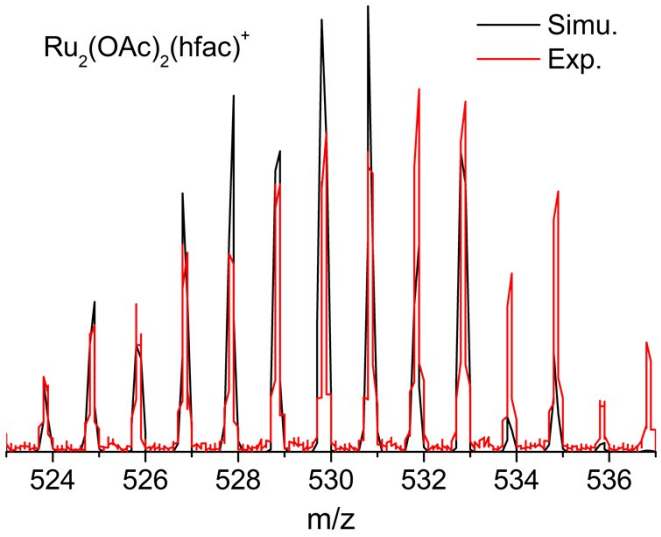

Fig. S14 The theoretical and experimental isotope distributions of species E.

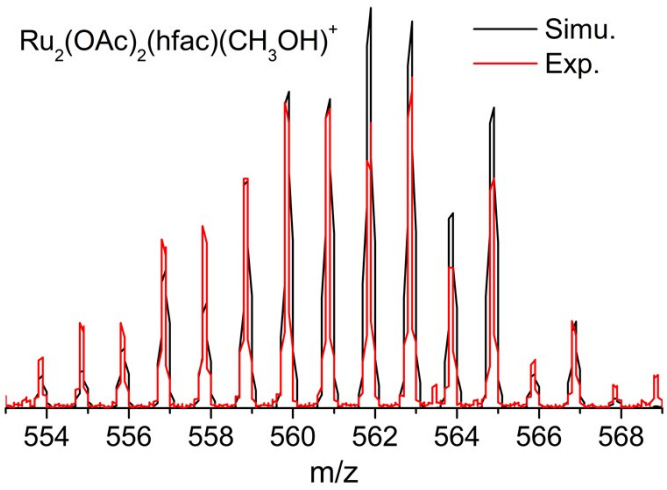

Fig. S15 The theoretical and experimental isotope distributions of species F.

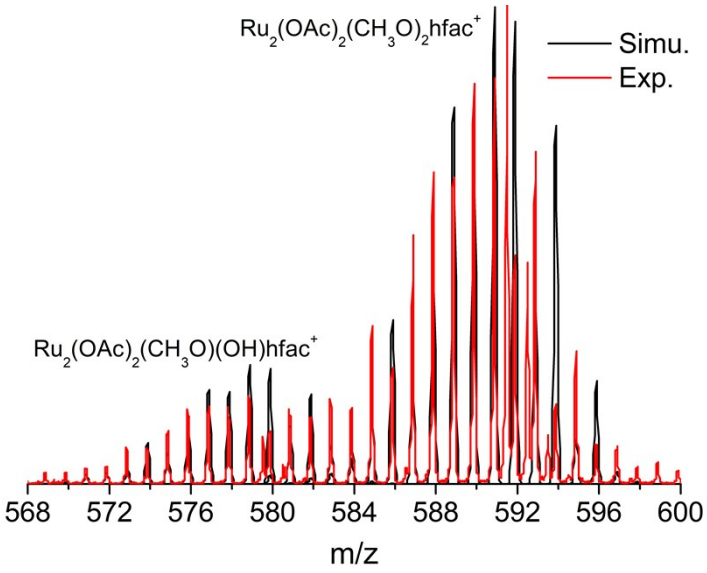

Fig. S16 The theoretical and experimental isotope distributions of species G and H.

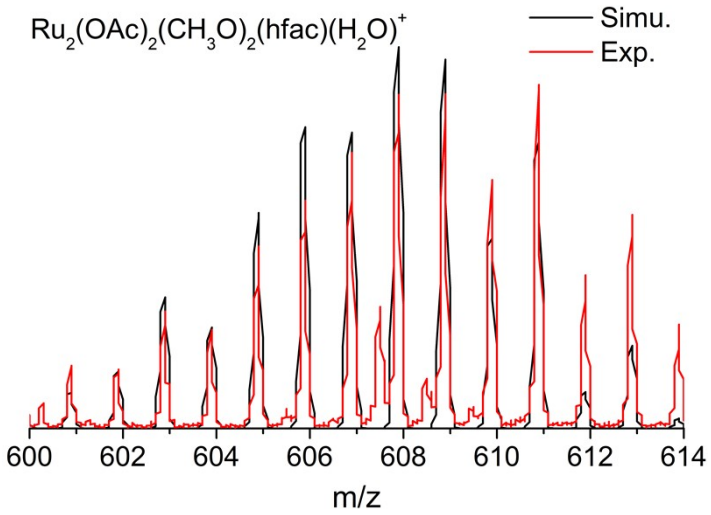

Fig. S17 The theoretical and experimental isotope distributions of species I.

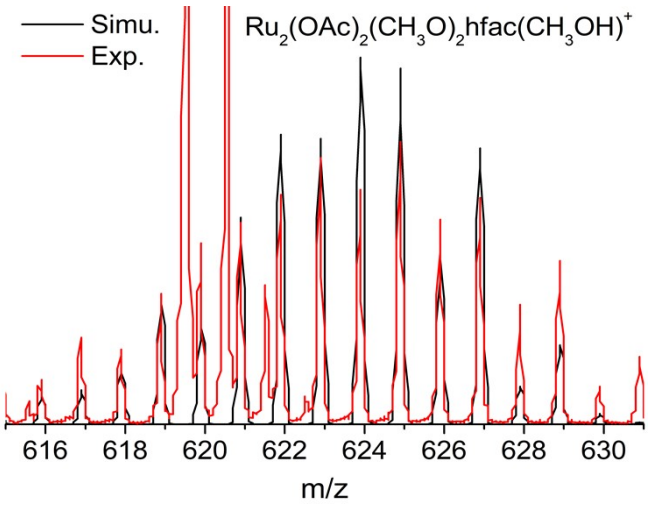

Fig. S18 The theoretical and experimental isotope distributions of species J.

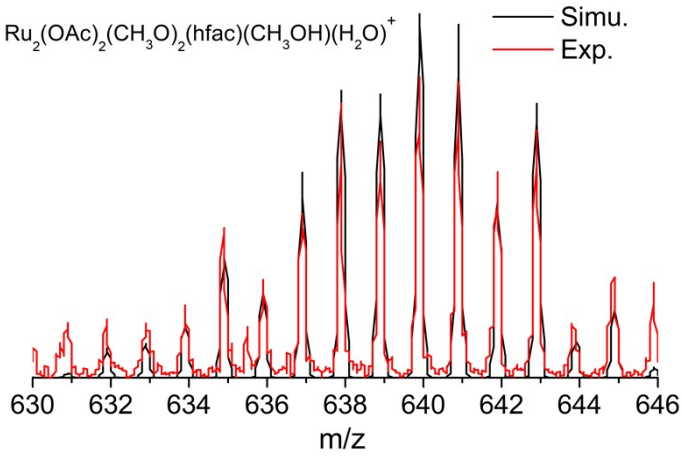

Fig. S19 The theoretical and experimental isotope distributions of species K.

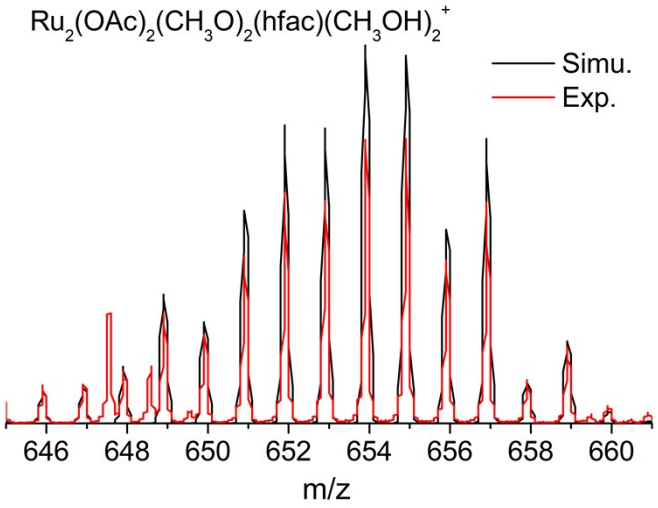

Fig. S20 The theoretical and experimental isotope distributions of species L.

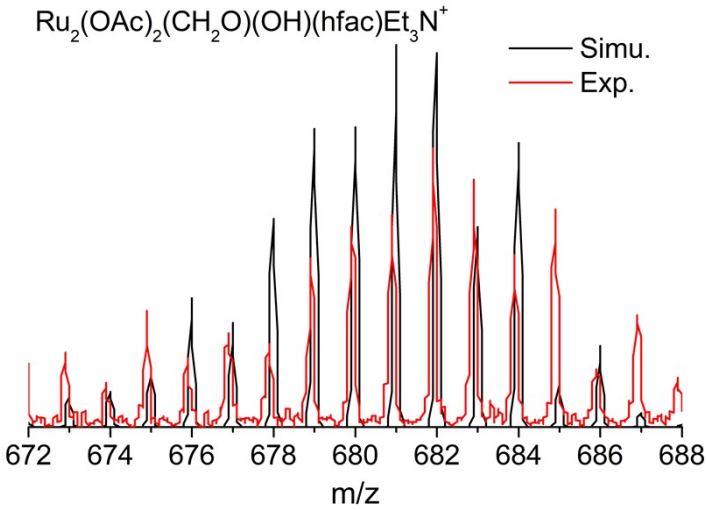

Fig. S21 The theoretical and experimental isotope distributions of species M.

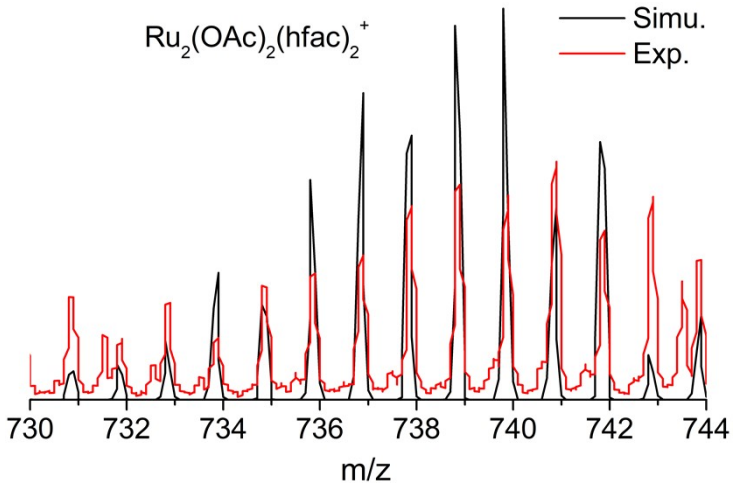

Fig. S22 The theoretical and experimental isotope distributions of species N.

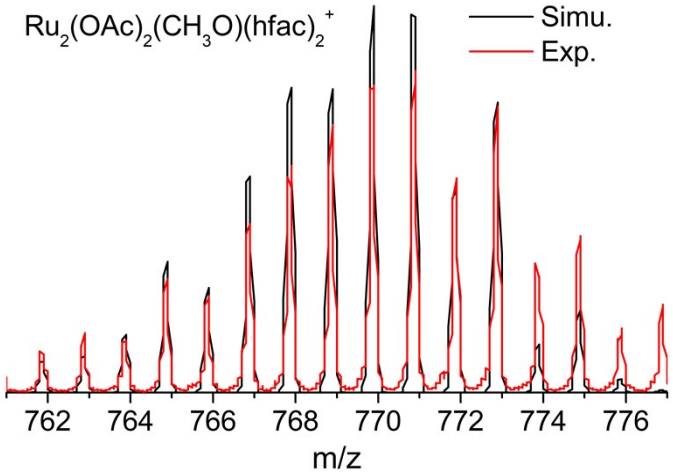

Fig. S23 The theoretical and experimental isotope distributions of species O.

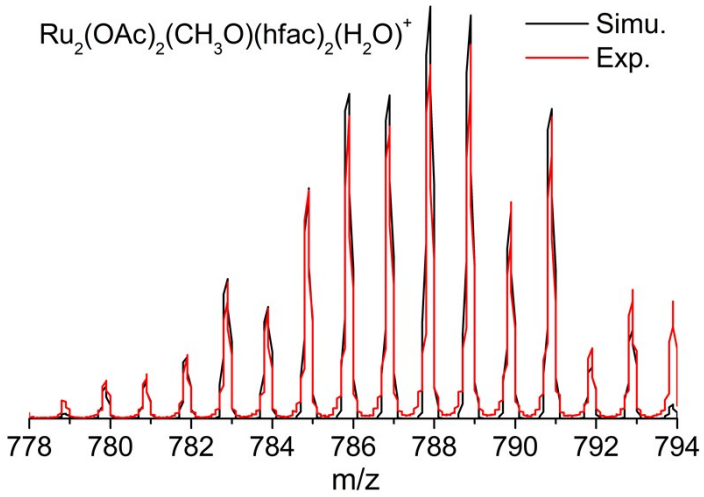

Fig. S24 The theoretical and experimental isotope distributions of species P.

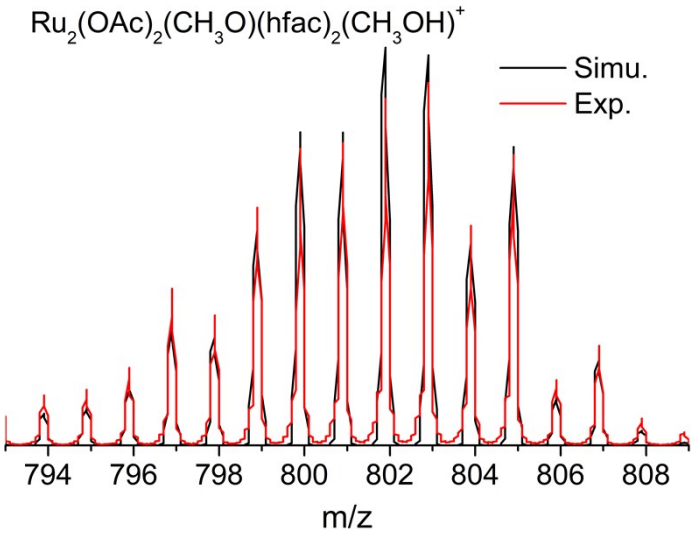

Fig. S25 The theoretical and experimental isotope distributions of species Q.

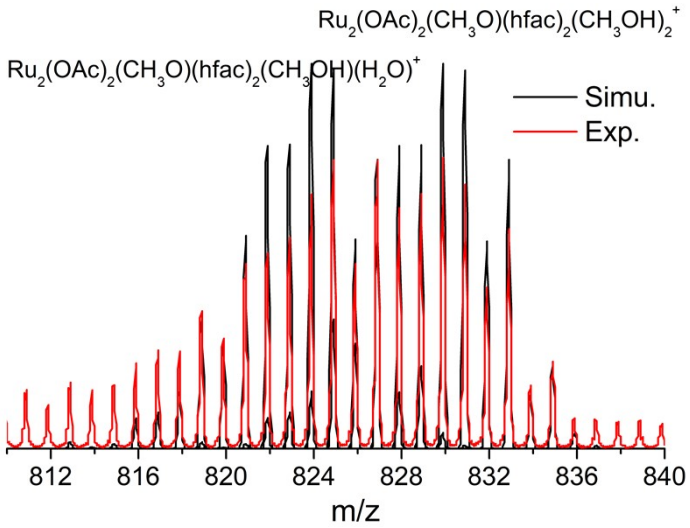

Fig. S26 The theoretical and experimental isotope distributions of species R.

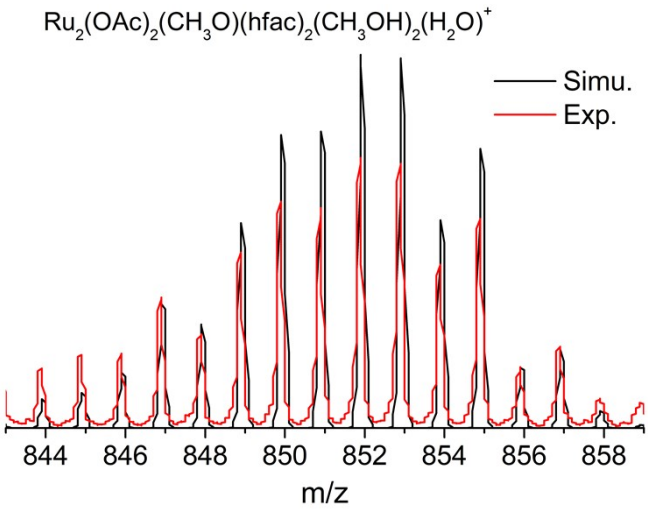

Fig. S27 The theoretical and experimental isotope distributions of species S.

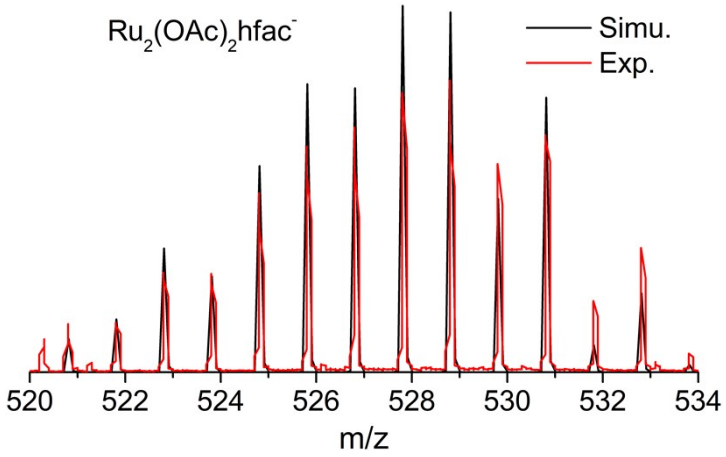

Fig. S28 The theoretical and experimental isotope distributions of species a

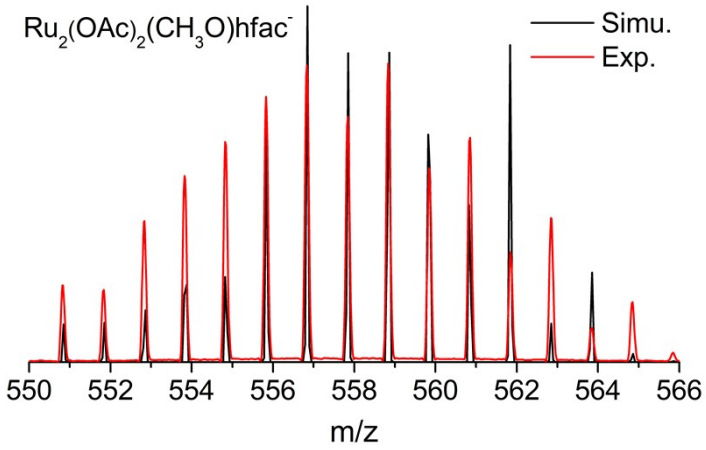

Fig. S29 The theoretical and experimental isotope distributions of species b

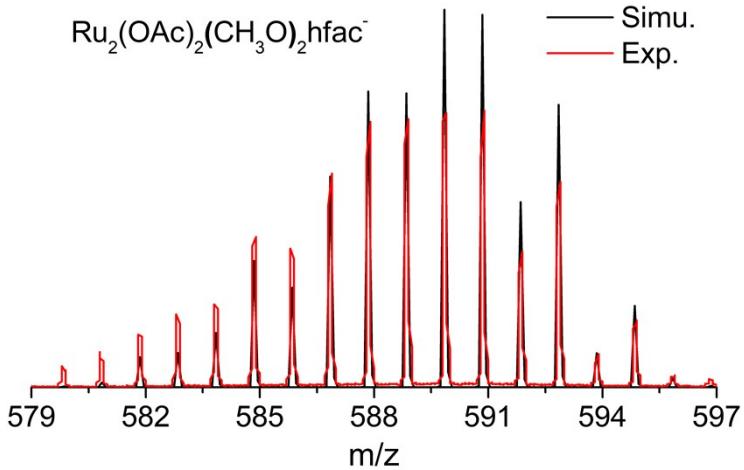

Fig. S30 The theoretical and experimental isotope distributions of species c.

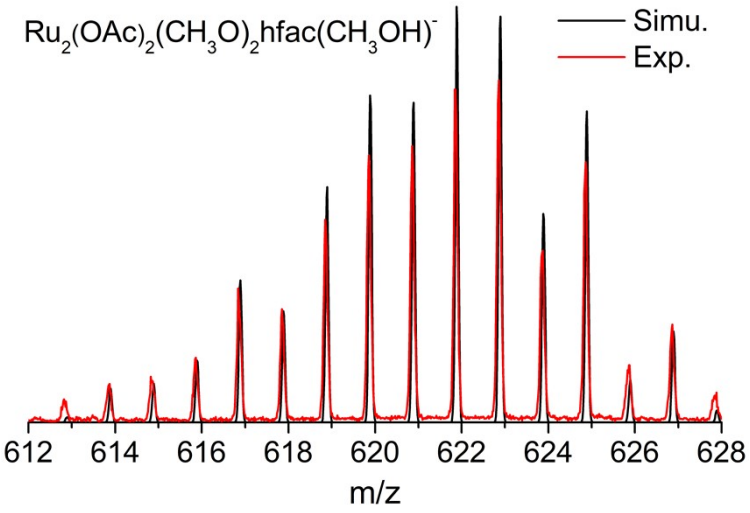

Fig. S31 The theoretical and experimental isotope distributions of species d.

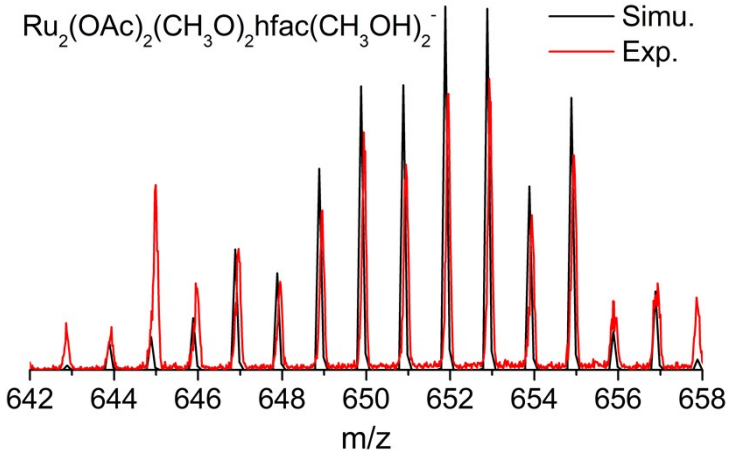

Fig. S32 The theoretical and experimental isotope distributions of species e.

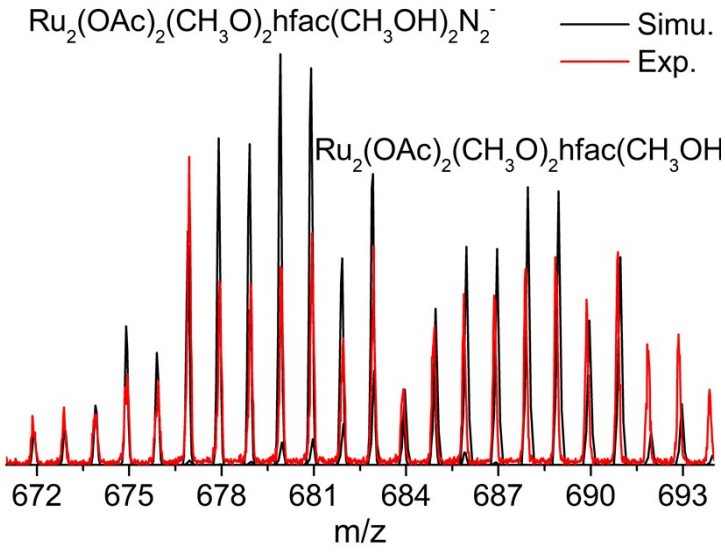

Fig. S33 The theoretical and experimental isotope distributions of species f. and g

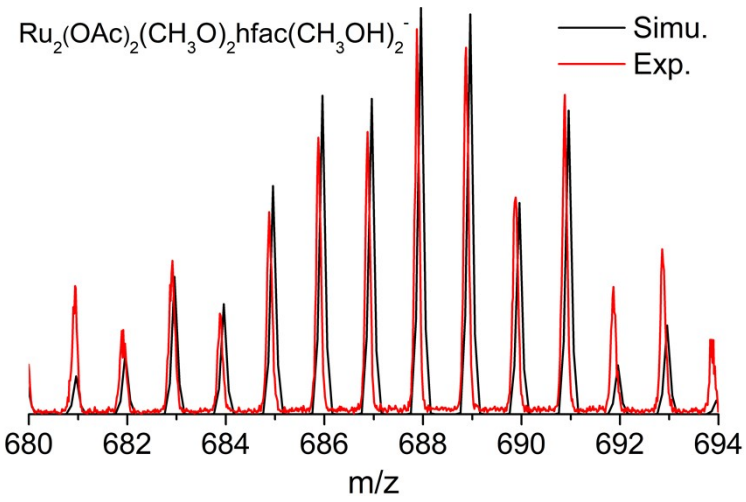

Fig. S34 The theoretical and experimental isotope distributions of species g.

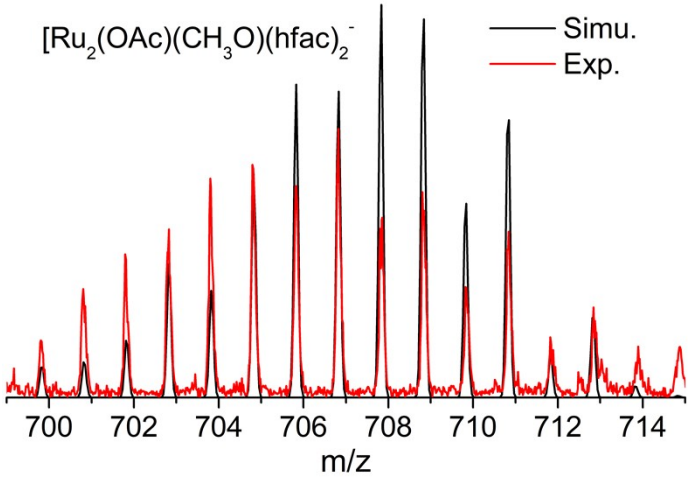

Fig. S35 The theoretical and experimental isotope distributions of species h.

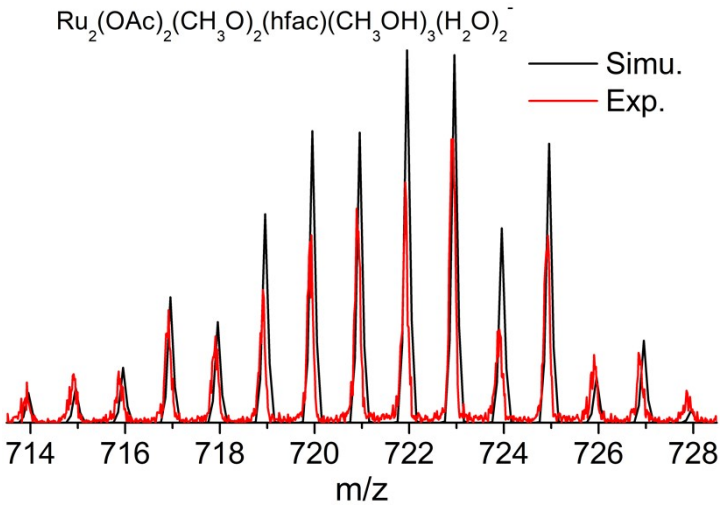

Fig. S36 The theoretical and experimental isotope distributions of species i.

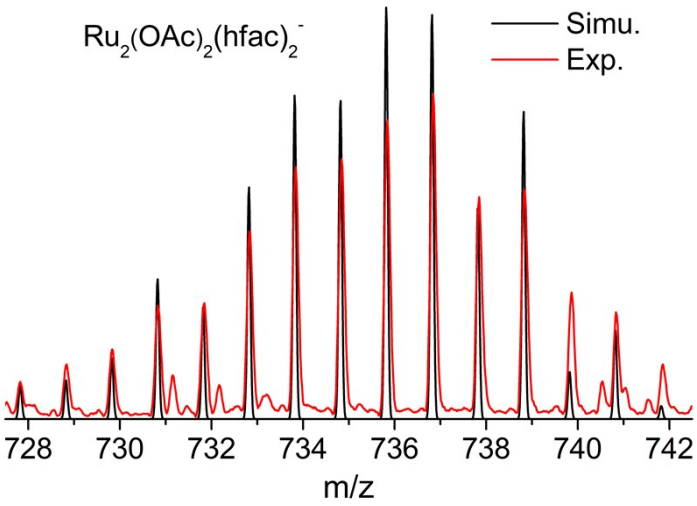

Fig. S37 The theoretical and experimental isotope distributions of species j.

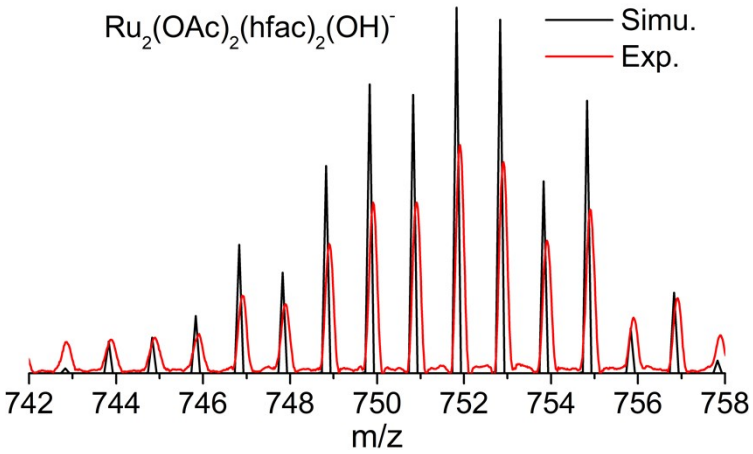

Fig. S38 The theoretical and experimental isotope distributions of species k.

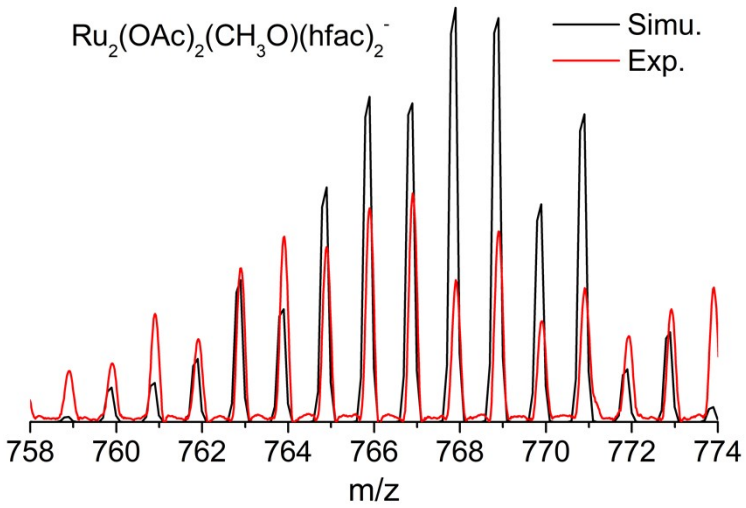

Fig. S39 The theoretical and experimental isotope distributions of species l.

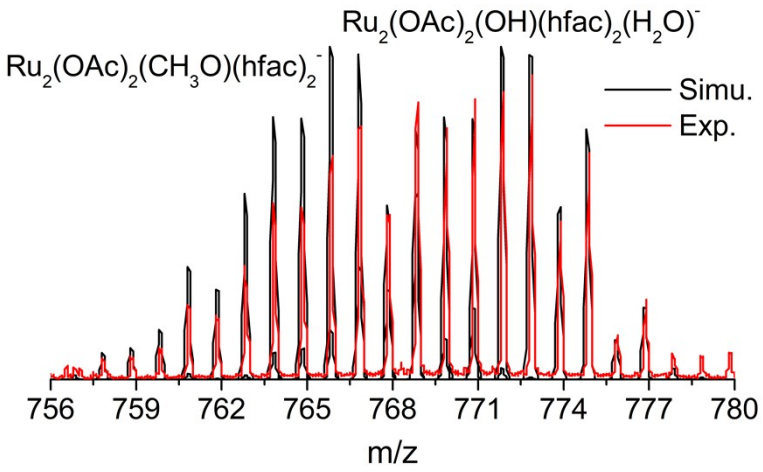

Fig. S40 The theoretical and experimental isotope distributions of species l and m.

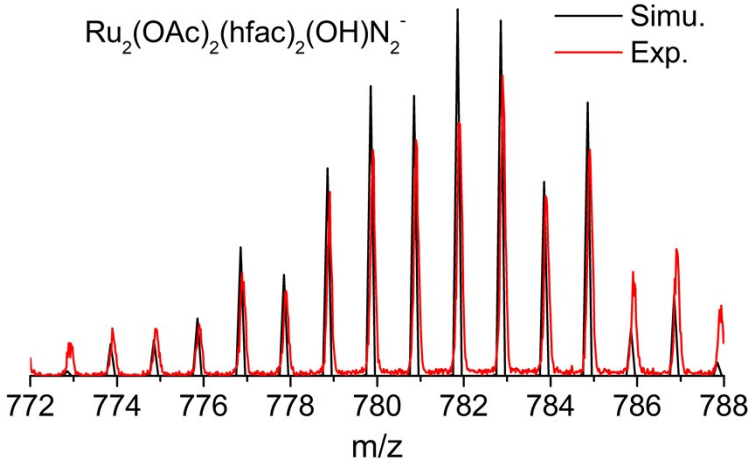

Fig. S41 The theoretical and experimental isotope distributions of species n.

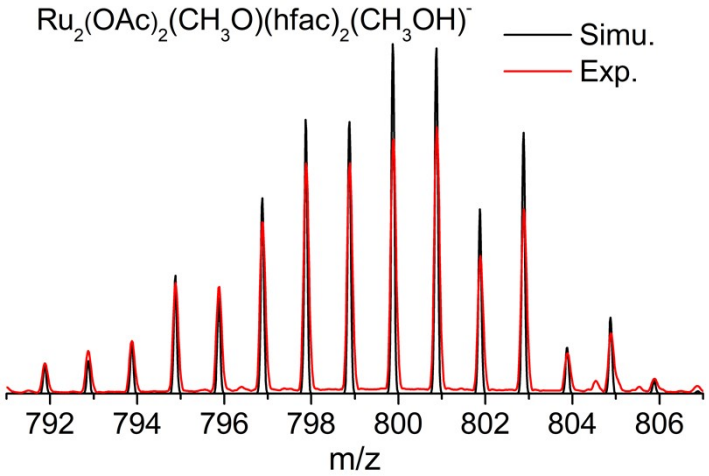

Fig. S42 The theoretical and experimental isotope distributions of species o.

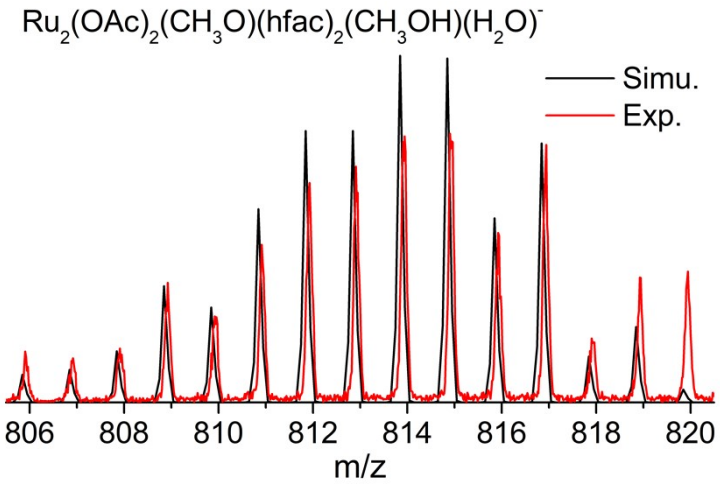

Fig. S43 The theoretical and experimental isotope distributions of species p.

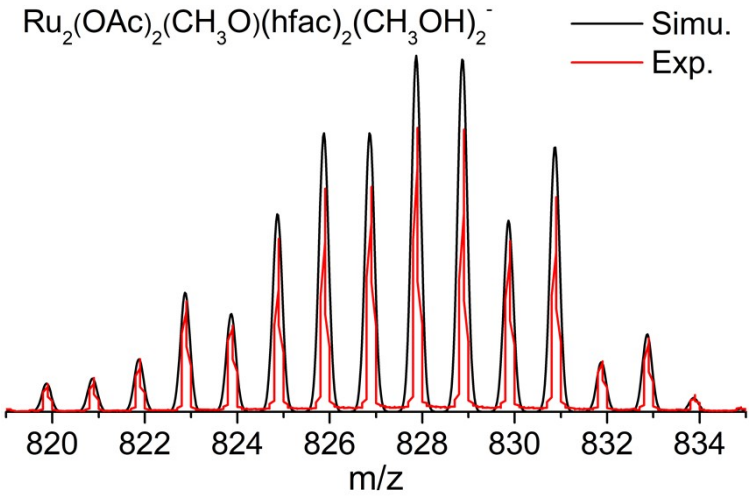

Fig. S44 The theoretical and experimental isotope distributions of species q.

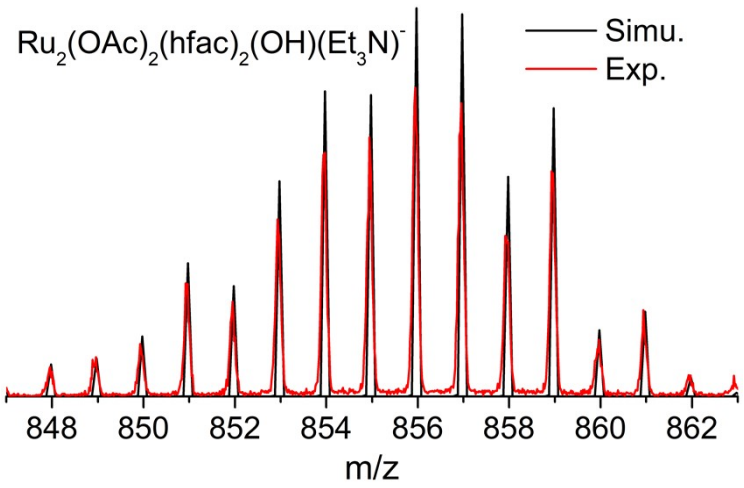

Fig. S45 The theoretical and experimental isotope distributions of species r.

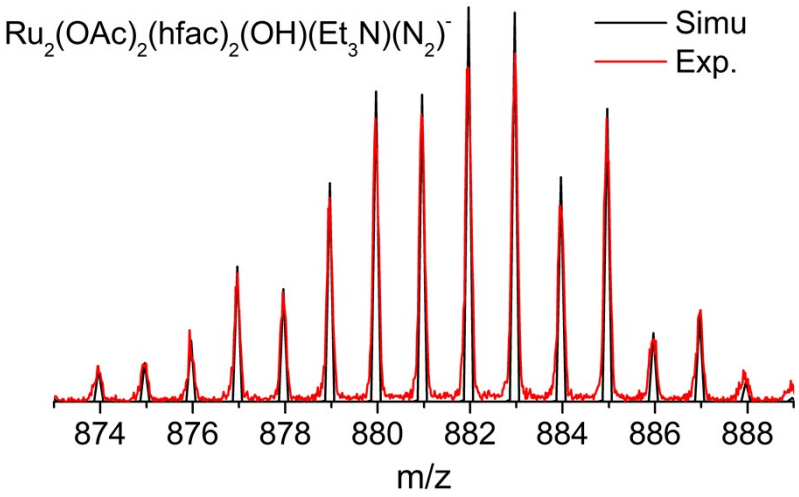

Fig. S46 The theoretical and experimental isotope distributions of species s.

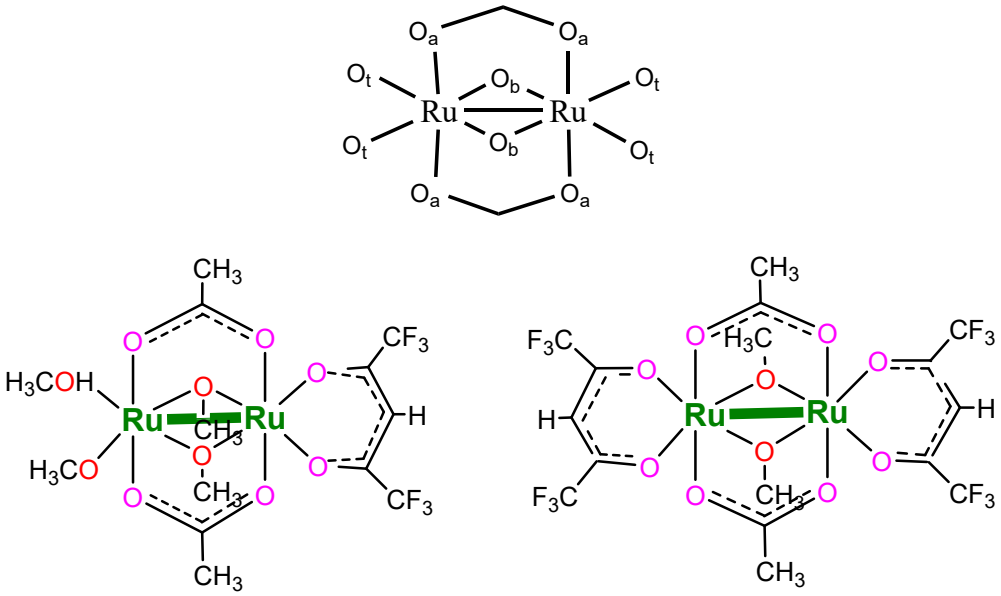

Table S8. Selected bond distances (Å) from the experiment and calculation of **1** and **2**.

Compound **1**			Compound **2**		
	Exp.	Calc.		Exp.	Calc.
Ru(1)–Ru(2)	2.468	2.532	Ru(1)–Ru(1A)	2.458	2.510
Ru(1)–O(2)	2.077	2.124	Ru(1)–O(1)	1.980	2.037
Ru(1)–O(4)	2.073	2.113	Ru(1)–O(2)	2.070	2.109
Ru(1)–O(6)	1.992	2.140	Ru(1)–O(3)	2.061	2.107
Ru(2)–O(3)	2.069	2.111	Ru(1)–O(4)	2.033	2.032
Ru(2)–O(5)	2.055	2.103	Ru(1)–O(5)	2.012	2.032
Ru(2)–O(7)	2.024	2.035	Ru(1A)–O(1)	1.983	2.038