Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Bis(acetylacetonato)bis(pyrazolato)Ruthenate(III) as a Redox-active Scorpionate Ligand

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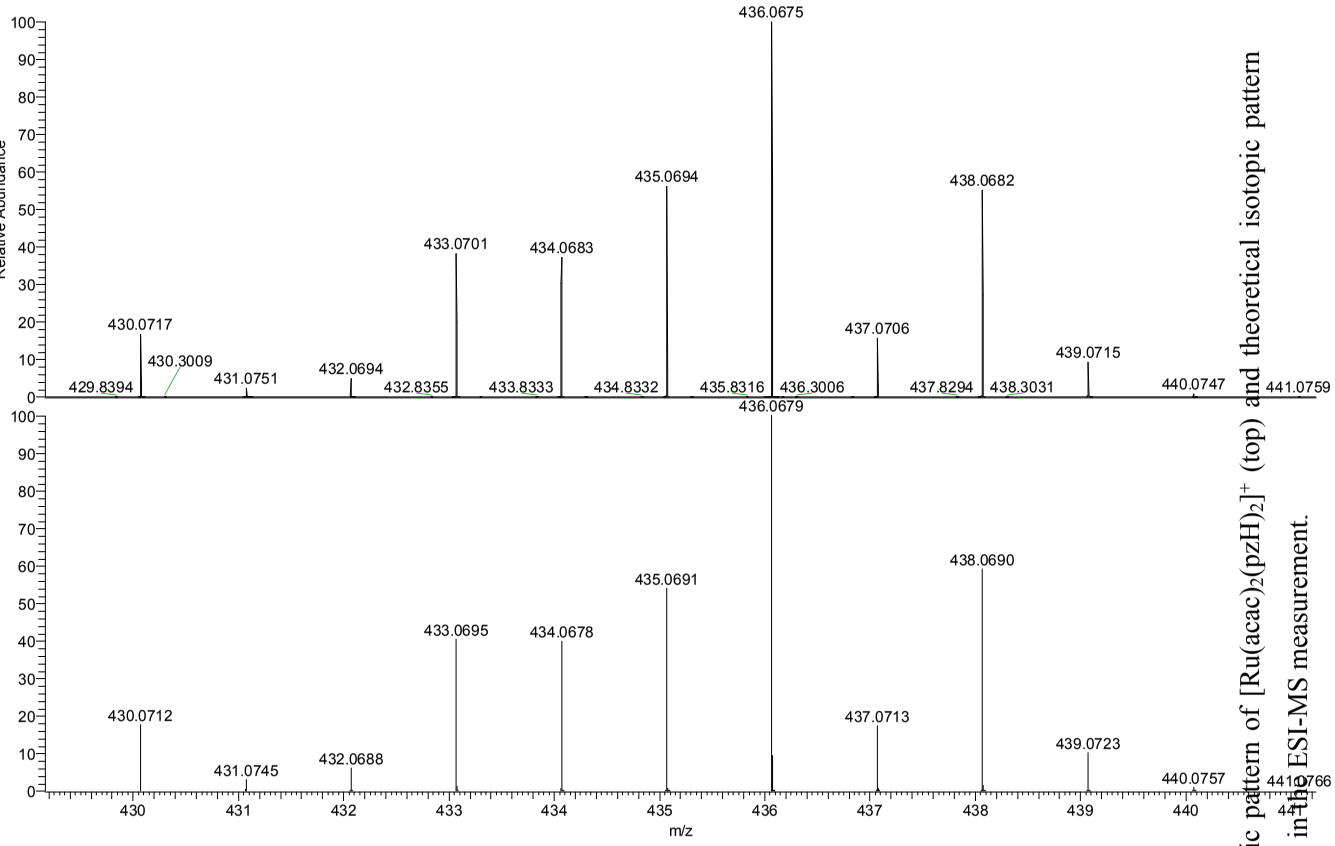

Fig. S1 Experimental isotropic pattern of $[Ru(acac)_2(pzH)_2]^+$ (top) and theoretical isotopic pattern for $[C_{16}H_{22}O_4N_4Ru]^+$ (bottom) in the ESI-MS measurement.

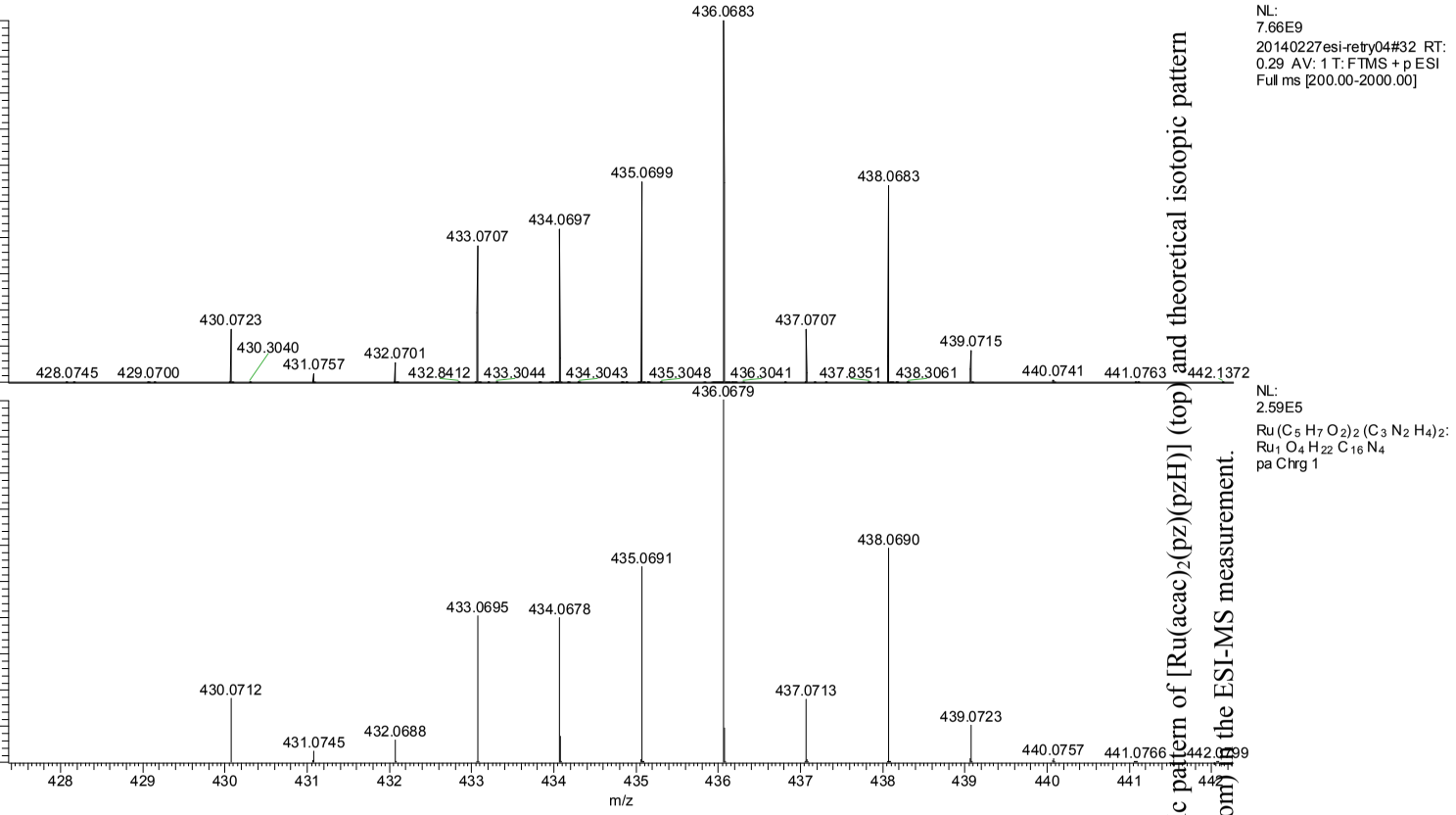

Fig. S2 Experimental isotropic pattern of [Ru(acac)$_2$(pz)(pzH)] (top) and theoretical isotopic pattern for [$C_{16}H_{21}O_4N_4Ru$+H]$^+$ (bottom) in the ESI-MS measurement.

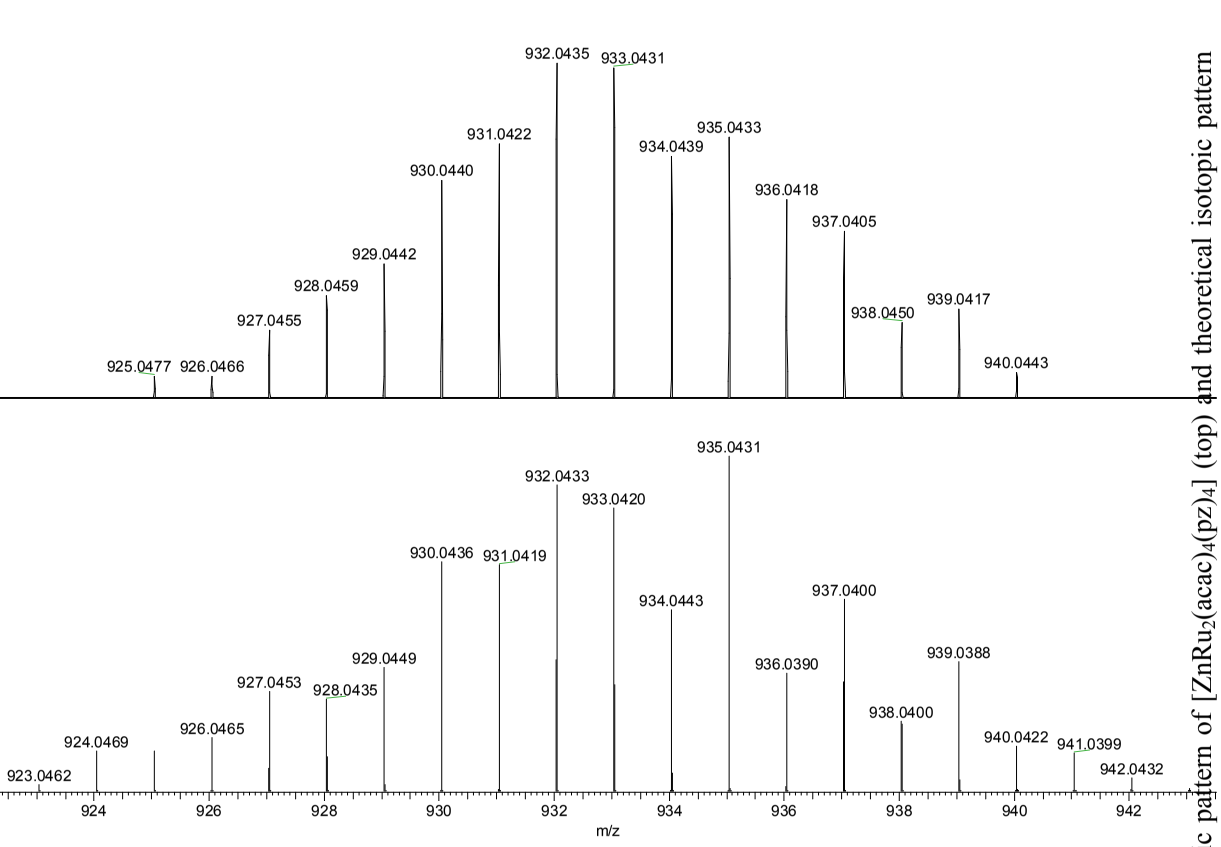

Fig. S3 Experimental isotropic pattern of $[ZnRu_2(acac)_4(pz)_4]$ (top) and theoretical isotopic pattern for $[C_{32}H_{40}N_8O_8Ru_2Zn+H]^+$ (bottom) in the ESI-MS measurement.

Fig. S4 Experimental isotropic pattern of $[Ru_3(acac)_4(CO)(pz)_4]$ (top) and theoretical isotopic patterns for $[C_{33}H_{40}N_8O_9Ru_3+H]^+$ (middle) and $[C_{33}H_{40}N_8O_9Ru_3+Na]^+$ (bottom) in the ESI-FT measurement.

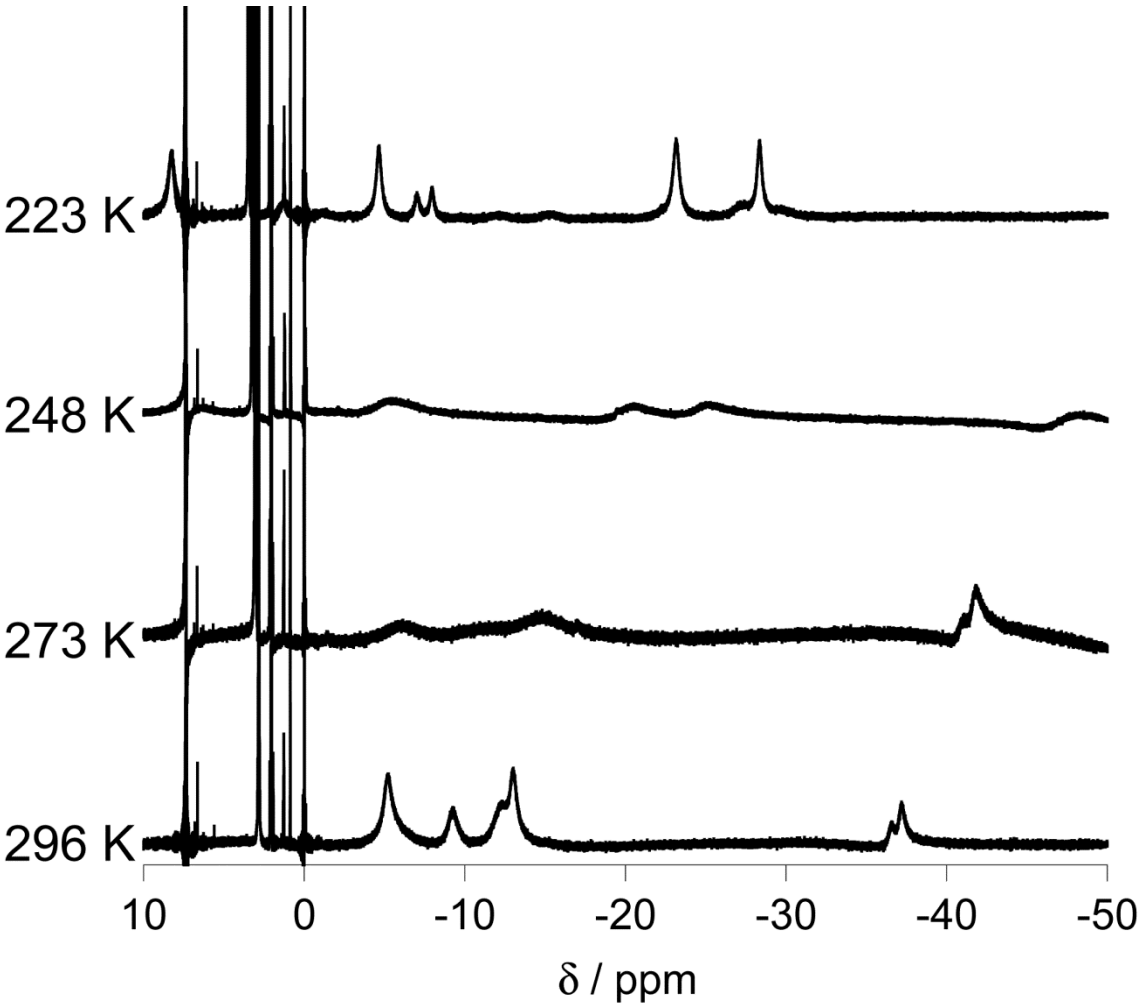

Fig. S5 NMR spectra of $[Ru_2Zn(acac)_4(pz)_4]$ (**2**) measured in acetone-d_6 in the range from 223 to 296 K.

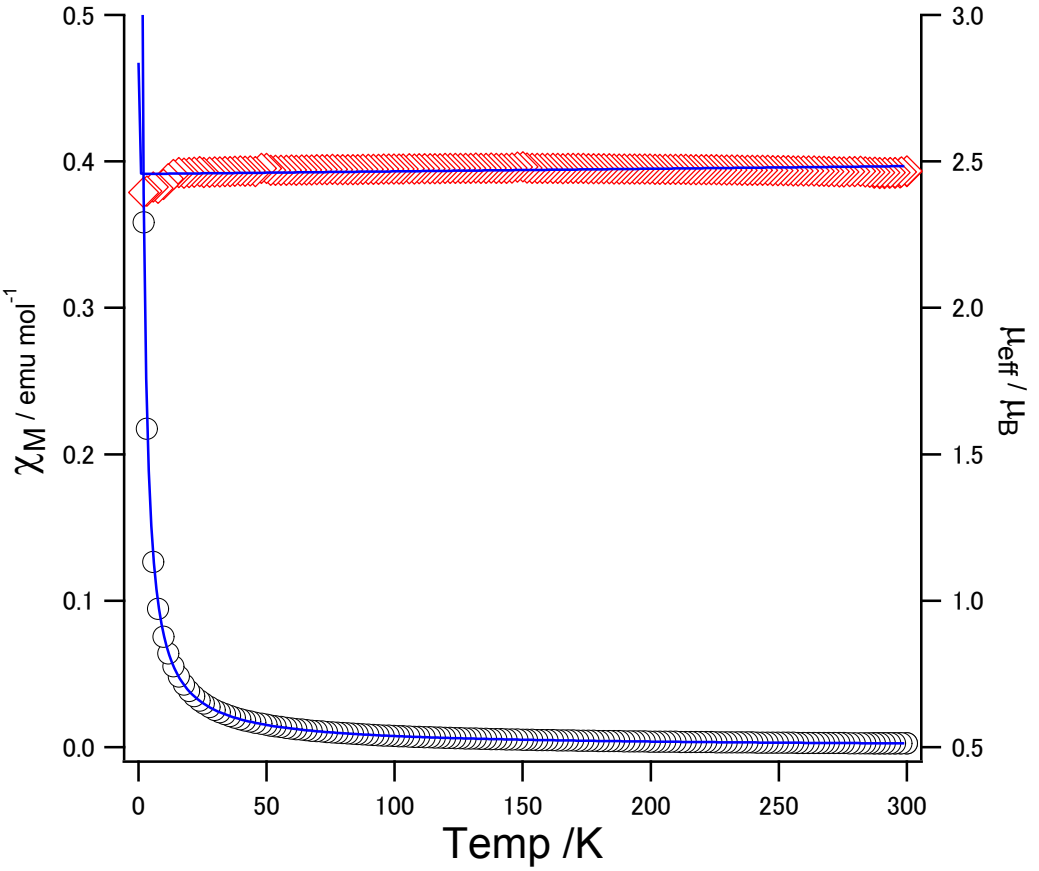

Fig. S6 Temperature dependence of the molar susceptibility (red circle) and magnetic moment (red rhomboid) for **2**. Solid lines is the result from least-squares fits using the Bleaney-Bowers equation: $\chi_M = \frac{Ng^2\beta^2}{kT}\left[\frac{1}{3+x^2}\right] + TIP, x = exp(\frac{-J}{kT})$. The terms *N*, *g*, *β*, k, J, and T in the above equation have the usual meaning and TIP means the temperature-independent paramagnetism. As a result of fitting, The parameters obtained from the fitting are g = 2.001, J = 0.018 cm^{-1}, TIP = 5.55 $\times 10^{-5}$ emu mol^{-1}.

Table S1 Selected bond lengths (Å) for **2** and **3**.

	Ru−O	Ru−N	M−N or C (M=Zn or Ru)	M···O (M=Zn or Ruo)
2	Ru1—O4 2.004 (3)	Ru1—N1 2.064 (4)	Zn1—N4 1.978 (5)	Zn1···O4 3.118 (5)
	Ru1—O2 2.015 (4)	Ru1—N3 2.013 (5)	Zn1—N5 1.978 (4)	Zn1···O5 3.107 (5)
	Ru1—O3 2.023 (4)	Ru2—N6 2.006 (5)	Zn1—N7 1.984 (4)	
	Ru1—O1 2.039 (4)	Ru2—N8 2.047 (4)	Zn1—N2 1.998 (5)	
	Ru2—O5 2.003 (3)			
	Ru2—O8 2.019 (3)			
	Ru2—O6 2.032 (4)			
	Ru2—O7 2.035 (4)			
3	Ru1—O2 1.996 (5)	Ru1—N4 2.001 (5)	Ru2—C17 1.809 (8)	Ru2−O4 2.235 (4)
	Ru1—O1 2.004 (5)	Ru1—N2 2.033 (6)	Ru2—N1 2.059 (6)	
	Ru1—O3 2.017 (5)	Ru3—N8 2.056 (5)	Ru2—N3 2.072 (5)	
	Ru1—O4 2.027 (4)	Ru3—N6 2.015 (6)	Ru2—N7 2.079 (5)	
			Ru2—N5 2.081 (6)	

Table S2 Selected angles (Å) for **2** and **3**.

	2	**3**
N−M−N (M=Zn or Ru)	N4—Zn1—N5 137.92 (19)	C17—Ru2—N1 89.6 (3)
	N4—Zn1—N7 103.22 (18)	C17—Ru2—N3 91.9 (3)
	N5—Zn1—N7 99.92 (18)	N1—Ru2—N3 86.6 (2)
	N4—Zn1—N2 100.12 (19)	C17—Ru2—N7 98.0 (3)
	N5—Zn1—N2 101.70 (18)	N3—Ru2—N7 89.6 (2)
	N7—Zn1—N2 114.25 (19)	C17—Ru2—N5 96.1 (3)
		N1—Ru2—N5 88.0 (2)
		N7—Ru2—N5 94.8 (2)
		N1—Ru2—O4 85.0 (2)
		N3—Ru2—O4 83.92 (18)
		N7—Ru2—O4 87.18 (18)
		N5—Ru2—O4 87.66 (19)

Table S3 Crystallographic and experimental data for [**1**H_2](PF_6), **1**H, **2**, and **3**.

Compound	[**1**H_2](PF_6)	**1**H	**2**	**3**
Formula	$C_{16}H_{22}N_4O_4RuPF_6$	$C_{16}H_{21}N_4O_4Ru$	$C_{32}H_{40}N_8O_8Ru_2Zn\cdot C_6H_6$	$C_{33}H40N_8O_9Ru_3\cdot 2(C_6H_6)$
Formula weight	580.42	434.44	1010.34	1152.16
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/n$	*P*n	$P2_1/c$
a / Å	9.0860 (7)	8.5206 (4)	8.4786 (11)	21.1904 (18)
b / Å	10.4112 (8)	26.7240 (13)	16.651 (2)	13.8632 (12)
c / Å	12.5088 (10)	8.9397 (5)	15.444 (2)	17.2910 (14)
α / °	90.739 (1)	90	90	90
β / °	104.555 (1)	113.796 (1)	92.841 (2)	107.780 (1)
γ / °	94.704 (1)	90	90	90
V / Å^3	1140.76 (15)	1862.56 (16)	2177.6 (5)	4836.9 (7)
Z	2	4	2	4
T / K	296	296	296	120
*D*x / Mg m^{-3}	1.69	1.549	1.541	1.582
Dimensions / mm	0.25, 0.19, 0.12	0.27, 0.24, 0.06	0.30, 0.20, 0.10	0.16, 0.15, 0.13
μ(Mo-Kα) / mm^{-1}	0.84	0.87	1.29	0.99
F(000)	582	884	1024	2328
Reflections collected	12838	21354	24846	41112
Unique reflections	5119	4297	9839	11042
Reflections with I > 2σ(I)	3985	3425	7054	6601
Parameters	293	230	492	582
GOF on F^2	1.04	1.04	0.97	1.04
[a]R_1 [$F^2 > 2\sigma(F^2)$]	0.049	0.031	0.042	0.061
[b]wR_2 (all data)	0.158	0.075	0.076	0.160
[C]Flack parameter	–	–	0.013(13)	–

[a]$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, [b]$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, [C]Flack, H. D., Acta Cryst. A, 1983, 39, 876-881.