Supporting information

Four-electron Oxidative Dehydrogenation Induced by Proton-coupled Electron Transfer in Ruthenium(III) Complex with 2-(1,4,5,6-Tetrahydropyrimidin-2-yl)phenolate

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Contents:

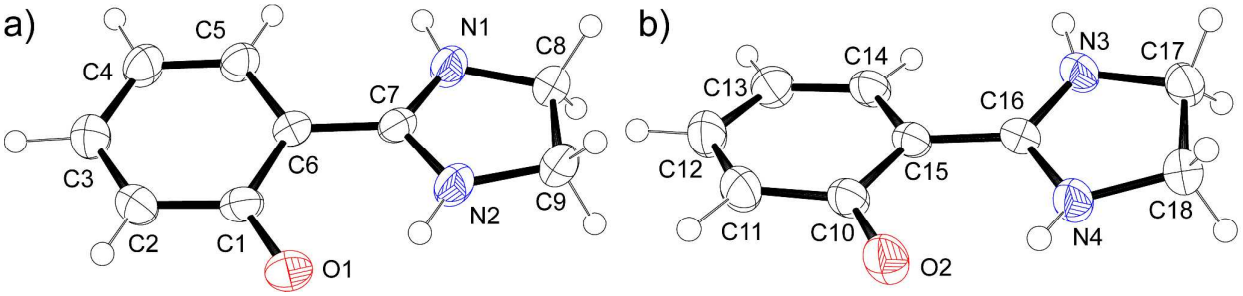

Figure S1. ORTEPs of H_2imn molecules (50% probability level). a) and b) are crystallographycally independent molecules.

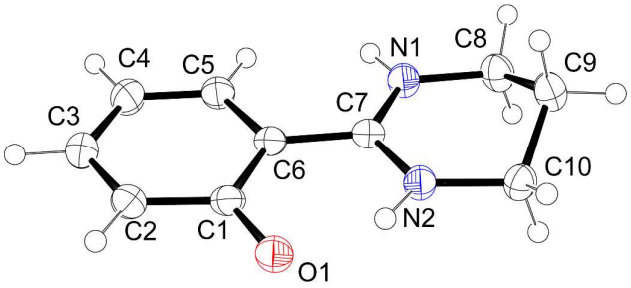

Figure S2. ORTEP of H_2thp molecule (50% probability level).

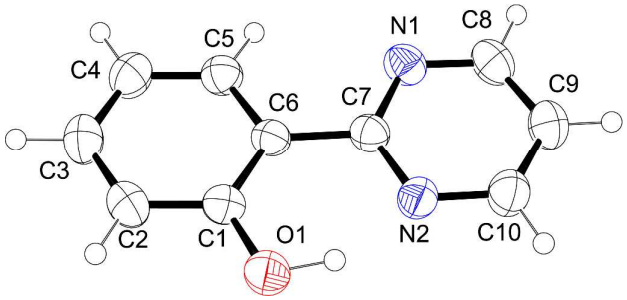

Figure S3. ORTEP of Hpym molecule (50% probability level).

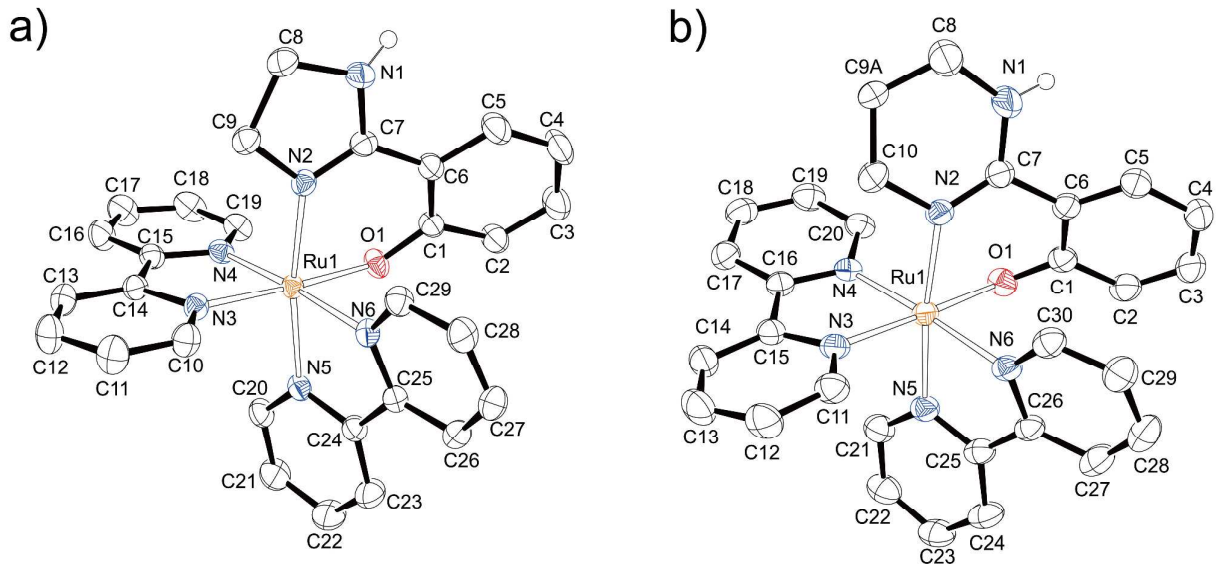

Figure S4. ORTEPs of Ru^{II} complexes a) $\mathbf{1}^{+}$ in $\mathbf{1}BF_4 \cdot CH_3OH$ and b) $\mathbf{2}^{+}$ in $\mathbf{2}BF_4 \cdot CH_3OH$ (50% probability level, H atom are omitted for clarity except for N–H atom). One of the possible positions of C9 atom (C9B) in $\mathbf{2}BF_4 \cdot CH_3OH$ was omitted.

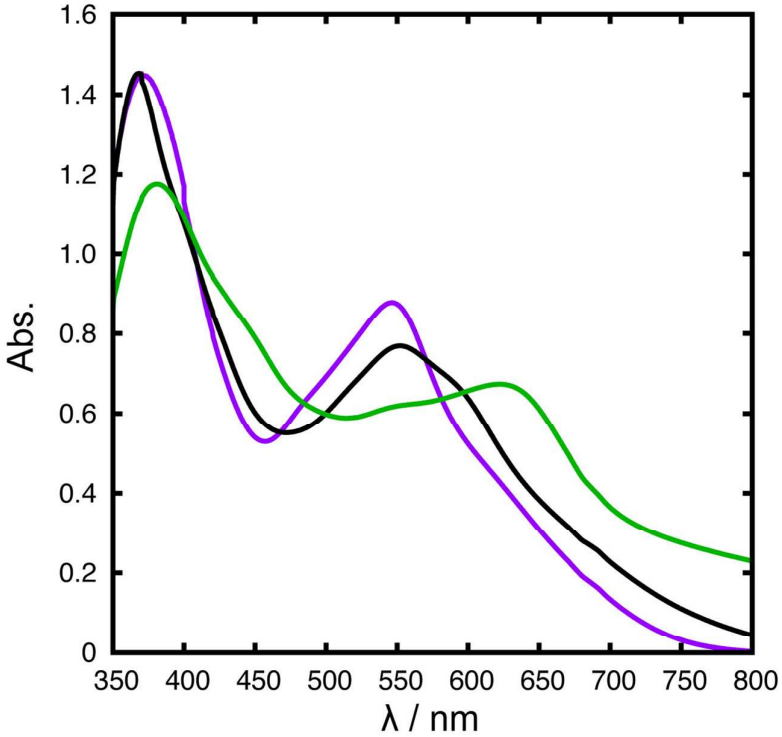

Figure S5. Absorption spectra of $\mathbf{1}BF_4$ (violet), with excess KO^{t}Bu (green) and after air exposure (black) in acetonitrile. The $\mathbf{1}BF_4$ solution is 1.0×10^{-4} M. The other solutions have the same concentration although exact values are uncertain.

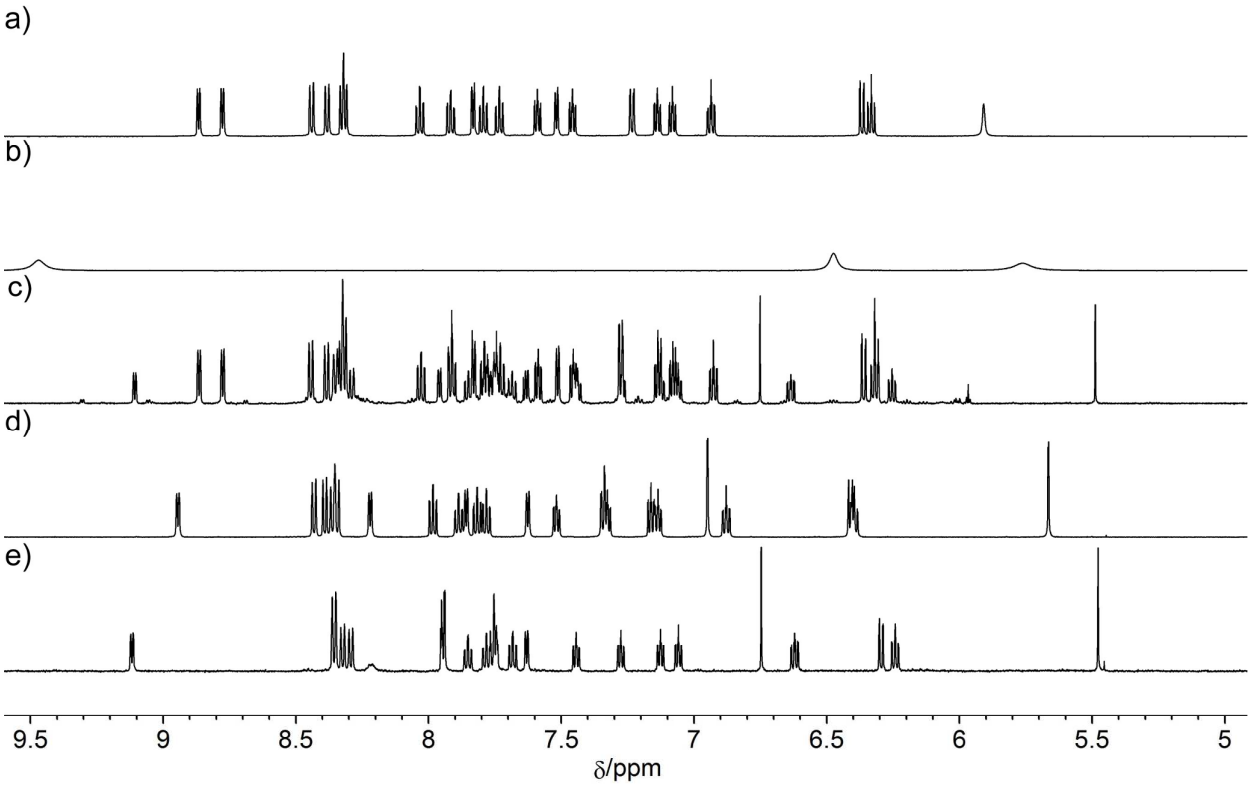

Figure S6. ^{1}H NMR spectra of a) **1**BF_4, b) **5**$(BF_4)_2$, c) **5**$(BF_4)_2$ with excess DBU, d) **3**BF_4 and e) **3**BF_4 with excess DBU (i.e. **7**) in CD_3CN.

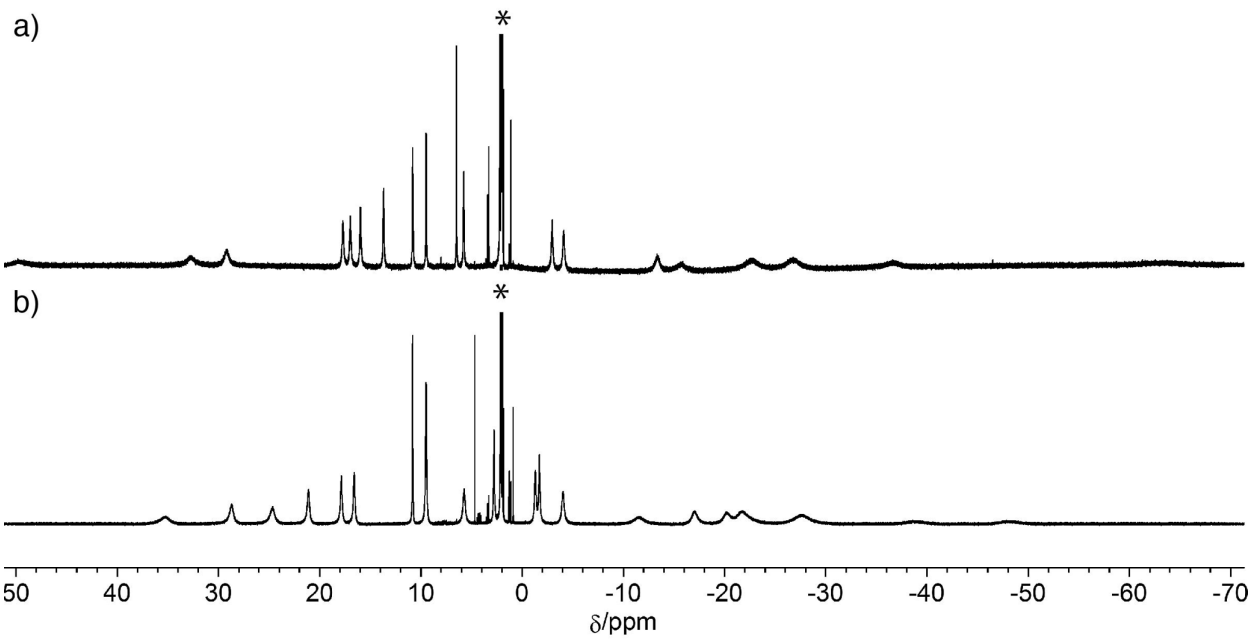

Figure S7. ^{1}H NMR spectra (–70-50 ppm) of a) **5**$(BF_4)_2$ and b) **6**$(BF_4)_2$ in CD_3CN. (* is assigned to residual solvent peak.)

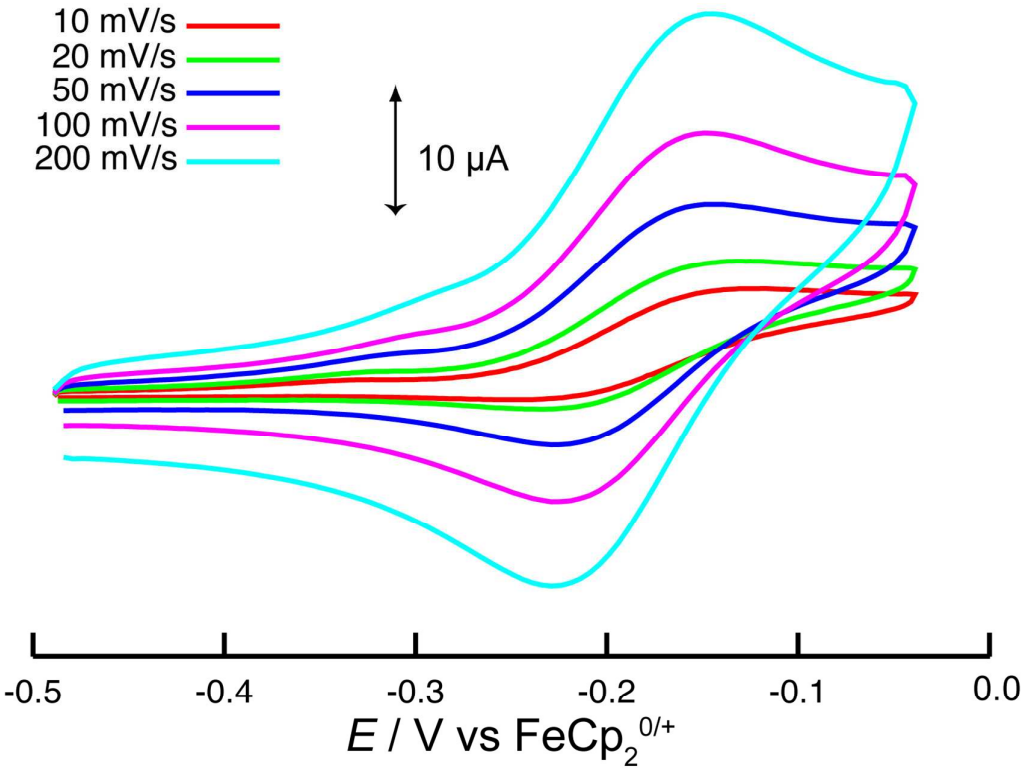

Figure S8. Scan rate dependent cyclic voltammograms of **6**$(BF_4)_2$ with 3 equiv. of DBU in acetonitrile.

pK_a determination of 3BF$_4$

UV-visible titration experiment was done using acetonitrile solution of [Ru^{II}(Himl)(bpy)$_2$]BF$_4$ (4.2×10^{-5} mol/L) and of DBU (1.7×10^{-1} mol/L). The pK_a value was derived from the following equation.

$$K_{eq} = \frac{[\mathbf{7}][\mathrm{HDBU}]}{[\mathbf{3}^+][\mathrm{DBU}]}$$

$$\frac{[\mathbf{7}][\mathrm{HDBU}]}{[\mathbf{3}^+]} = K_{eq}[\mathrm{DBU}], \quad \frac{[\mathbf{7}]}{[\mathbf{3}^+]} = \frac{A - A_3}{A_7 - A}$$

$$\mathrm{p}K_{a(3)} = \mathrm{p}K_{a(\mathrm{HDBU})} - \log K_{eq}$$

A_3 and A_7 are the absorbance of pure **3**BF$_4$ and **3**BF$_4$ with 20 equiv. of DBU. p$K_{a(\mathbf{3})}$ and p$K_{a(\mathrm{HDBU})}$ is the pK_a value for **3**BF$_4$ and HDBU[1] (24.13) in acetonitrile, respectively. Plots of [**7**][HDBU] vs. [DBU] at three different wavelengths (587, 538 and 429 nm) are shown below. The slopes of each linear plot, K_{eq}, are 0.979, 1.193 and 1.090 (R^2 = 0.99876, 0.99063 and 0.99663, respectively). From these values, p$K_{a(\mathbf{3})}$ was determined to be 24.1.

[1] Kaljurand, I.; Rodima, T.; Leito, I.; Koppel, I.; Schwesinger, R. *J. Org. Chem.* **2000**, *65*, 6202–8.

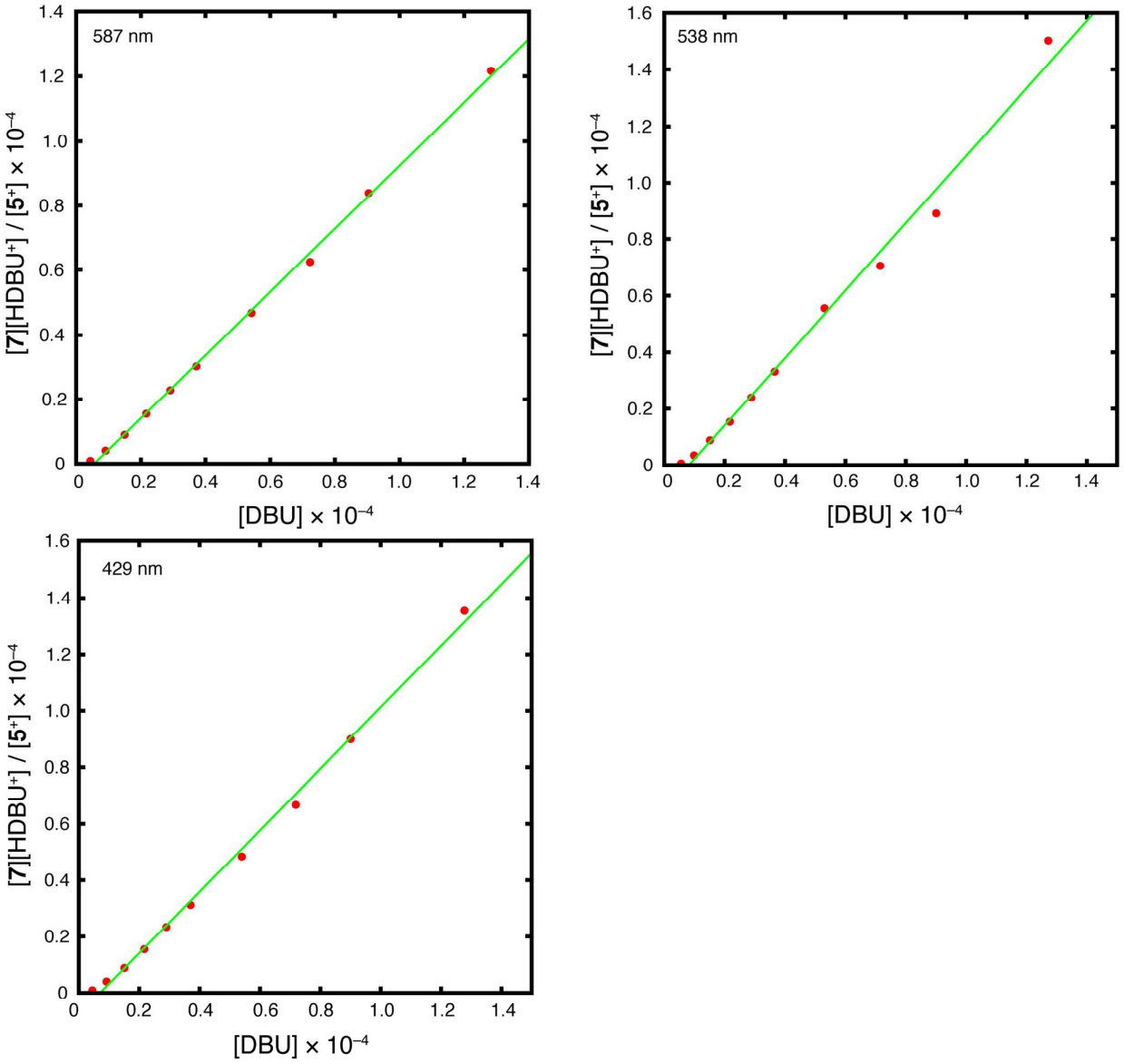

Figure S9. Plots of [**7**][HDBU] vs. [DBU] from UV–vis titration experiment at three different wavelength (587, 538, 429 nm).

Table S1. Crystallographic data for the complexes.

Complex	**1**BF_4·CH_3OH	**2**BF_4·CH_3OH	**3**Cl·2CH_3CN	**4**BF_4	**5**$(BF_4)_2$	**6**$(BF_4)_2$	**7**·CH_3CN
Chemical formula	$C_{30}H_{29}BF_4N_6O_2Ru$	$C_{31}H_{31}BF_4N_6O_2Ru$	$C_{33}H_{29}ClN_8ORu$	$C_{30}H_{23}BF_4N_6ORu$	$C_{29}H_{25}B_2F_8N_6ORu$	$C_{32}H_{27}B_2F_8N_6ORu$	$C_{31}H_{25}N_7ORu$
Formula weight	693.47	707.5	690.17	671.42	748.23	762.26	612.65
Color and shape of crystal	violet, block	black, block	violet, prism	red, platelet	violet, platelet	brown, platelet	Violet, prism
Size of specimen (mm^3)	0.40 × 0.30 × 0.30	0.50 × 0.40 × 0.40	0.10 × 0.05 × 0.05	0.10 × 0.10 × 0.05	0.25 × 0.20 × 0.10	0.30 × 0.20 × 0.10	0.08 × 0.08 × 0.04
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$Pna2_1$
a / Å	10.3264(7)	9.9379(7)	15.013(7)	7.754(2)	21.063(2)	21.305(2)	9.881(10)
b / Å	13.1097(7)	10.0441(8)	9.100(4)	10.279(3)	10.210(1)	10.1333(6)	27.42(3)
c / Å	22.144(2)	30.4265(19)	22.073(9)	17.134(5)	14.430(2)	14.584(1)	9.803(10)
α / °	90.000	90.000	90.000	95.990(3)	90.000	90.000	90.000
β / °	94.612(2)	95.0059(18)	94.156(5)	96.674(5)	98.204(3)	100.059(2)	90.000
γ / °	90.000	90.000	90.000	90.762(4)	90.000	90.000	90.000
V / $Å^3$	2988.0(3)	3025.5(4)	3007(3)	1348.5(7)	3071.3(5)	3100.0(4)	2656(5)
Z	4	4	4	2	4	4	4
T / K	191	193	103	193	192	193	103
D_{calc}/ g cm^{-3}	1.541	1.553	1.524	1.653	1.618	1.633	1.532
F (000)	1408	1440	1408	676	1500	1532	1248
μ(Mo-K$_\alpha$) / cm^{-1}	5.889	5.833	6.524	6.471	5.946	5.907	6.299
R_{int}	0.0192	0.0300	0.1705	0.0332	0.0808	0.0362	0.1235
$2\theta_{max}$/ °	54.9	55.0	55.0	55.0	54.0	55.0	54.9
No. of independent refrection	6829	6909	6882	6078	6991	7088	5991
$R_1(F^2: F_o^2 > 2\sigma(F_o^2))$	0.0283	0.0358	0.0827	0.0308	0.0516	0.0292	0.0888
$wR_2(F^2$: all data)	0.0824	0.0977	0.1515	0.0806	0.1306	0.0770	0.1630

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

Table S2. Crystallographic data for the ligand precursors.

Ligand precursor	H_2imn	H_2thp	Hpym
Chemical formula	$C_9H_{10}N_2O$	$C_{10}H_{12}N_2O$	$C_{10}H_8N_2O$
Formula weight	162.19	176.22	172.19
Color and shape of crystal	colorless, platelet	colorless, block	colorless, block
Size of specimen (mm^3)	0.50 × 0.40 × 0.30	0.40 × 0.20 × 0.10	0.30 × 0.25 × 0.20
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a / Å	9.947(2)	9.790(2)	7.446(2)
b / Å	7.457(2)	7.1703(9)	9.622(2)
c / Å	21.436(4)	12.654(2)	11.538(3)
α / °	90.000	90.000	90.000
β / °	96.718(6)	101.326(3)	98.594(6)
γ / °	90.000	90.000	90.000
V / $Å^3$	1579.2(5)	870.9(2)	817.4(3)
Z	8	4	4
T / K	193	188	192
D_{calc}/ g cm^{-3}	1.364	1.344	1.399
F (000)	688	376	360
μ(Mo-K_α) / cm^{-1}	0.919	0.891	0.938
R_{int}	0.0559	0.0301	0.0480
$2\theta_{max}$/ °	55.0	55.0	54.9
No. of independent refrection	3608	1999	1871
$R_1(F^2: F_o^2 > 2\sigma(F_o^2))$	0.0431	0.0410	0.0465
$wR_2(F^2$: all data)	0.1211	0.1223	0.1410

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

Table S3. Bond distances of the Ru complexes around Ru center and N1–C7–N2 (Å).

	1BF_4·CH_3OH	**2**BF_4·CH_3OH	**3**Cl·2CH_3CN	**4**BF_4	**5**$(BF_4)_2$	**6**$(BF_4)_2$	**7**·CH_3CN
Ru–O1	2.0763(18)	2.0673(14)	2.060(4)	2.0911(16)	1.9874(15)	2.011(3)	2.112(6)
Ru–N2	2.095(2)	2.0589(16)	2.066(5)	2.0826(19)	2.0353(17)	1.997(3)	2.088(8)
Ru–N3	2.033(2)	2.0312(16)	2.031(5)	2.0317(19)	2.0514(17)	2.045(3)	2.058(7)
Ru–N4	2.037(2)	2.0384(16)	2.031(5)	2.0413(18)	2.0362(16)	2.044(3)	2.078(7)
Ru–N5	2.044(2)	2.0440(17)	2.044(5)	2.0356(19)	2.1015(17)	2.099(3)	2.078(8)
Ru–N6	2.066(2)	2.0428(17)	2.050(5)	2.0496(18)	2.0857(15)	2.089(3)	2.072(7)
N1–C7	1.359(3)	1.368(3)	1.362(8)	1.340(3)	1.340(3)	1.330(6)	1.369(12)
N2–C7	1.310(3)	1.302(3)	1.344(8)	1.369(3)	1.322(3)	1.324(5)	1.391(10)