

Donor atom preference of organoruthenium and –rhodium cations on the interaction with novel ambidentate (N,N) and (O,O) chelating ligands in aqueous solution

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Supporting information

Table S1. Crystallographic parameters and refinement details for H(L1) and H(L2).

Chemical formula	C ₉ H ₁₄ N ₂ O ₂ ·3(H ₂ O) (H(L1))	C ₁₄ H ₁₇ N ₃ O ₂ (H(L2))
M_r	236.27	259.30
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Temperature (K)	295	293
a, b, c (Å)	7.7713 (3), 8.3192 (4), 10.1279 (4)	9.4186 (8), 8.2937 (6), 17.7160 (14)
α, β, γ (°)	104.400 (2), 90.021 (2), 94.129 (2)	99.534 (3)
V (Å ³)	632.45 (5)	1364.77 (19)
Z	2	4
Radiation type	Mo $K\alpha$	
μ (mm ⁻¹)	0.10	0.09
Crystal size (mm)	0.75 × 0.39 × 0.14	0.19 × 0.18 × 0.15
Diffractometer	Bruker D8 VENTURE	
Absorption correction	Multi-scan <i>SADABS2016/2</i> - Bruker AXS area detector scaling and absorption correction	
T_{\min}, T_{\max}	0.60, 0.99	0.87, 0.99
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14222, 2492, 2036	12415, 2572, 1860
R_{int}	0.079	0.058
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.618	0.609
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.076, 0.230, 1.07	0.049, 0.123, 1.05
No. of reflections	2492	2572
No. of parameters	173	175
No. of restraints	10	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	
$(\Delta/\sigma)_{\text{max}}$	0.001	0.001
$\Delta_{\text{max}}, \Delta_{\text{min}}$ (e Å ⁻³)	0.68, -0.31	0.19, -0.18

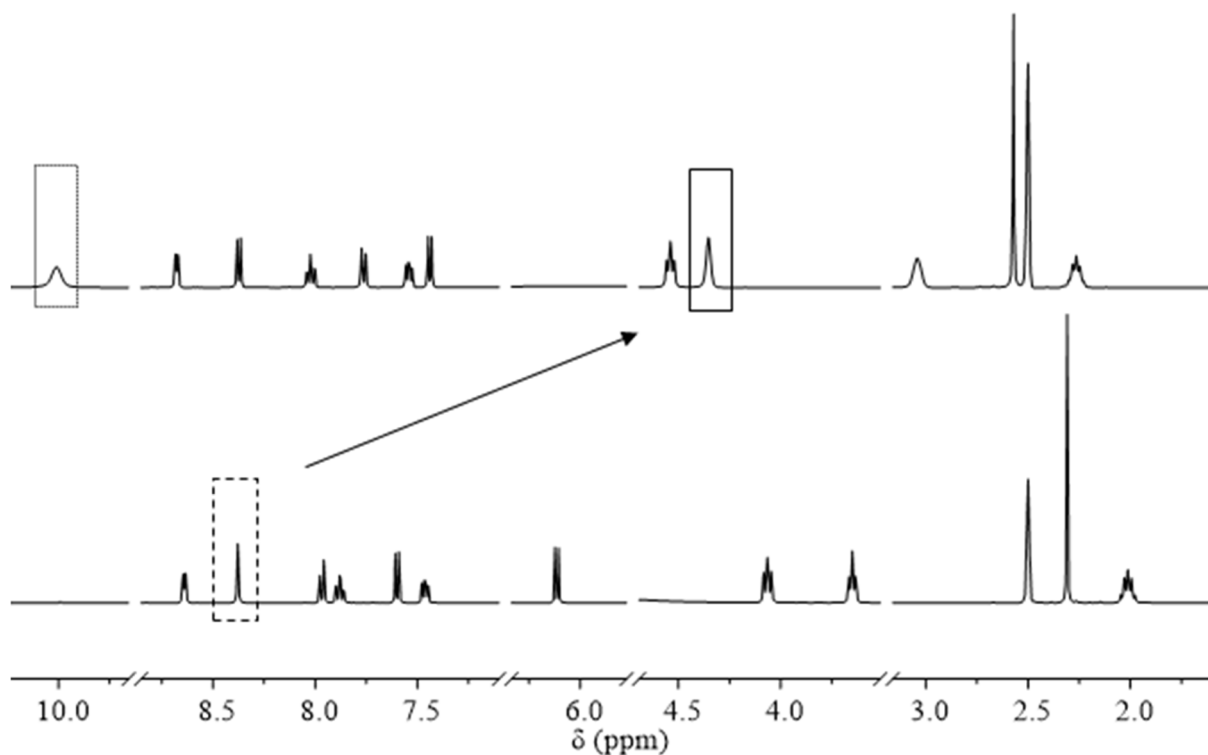


Figure S1. ^1H NMR spectrum of H(L4) (below) and H(L5)·2 HCl (above) in $\text{d}^6\text{-DMSO}$. The appearance of the signal belonging to the NH_2 protons (10.01 ppm; dotted) in the aromatic and that of CH_2 (4.35 ppm; solid) in the aliphatic region of the H(L5)·2 HCl spectrum indicates a successful reduction.

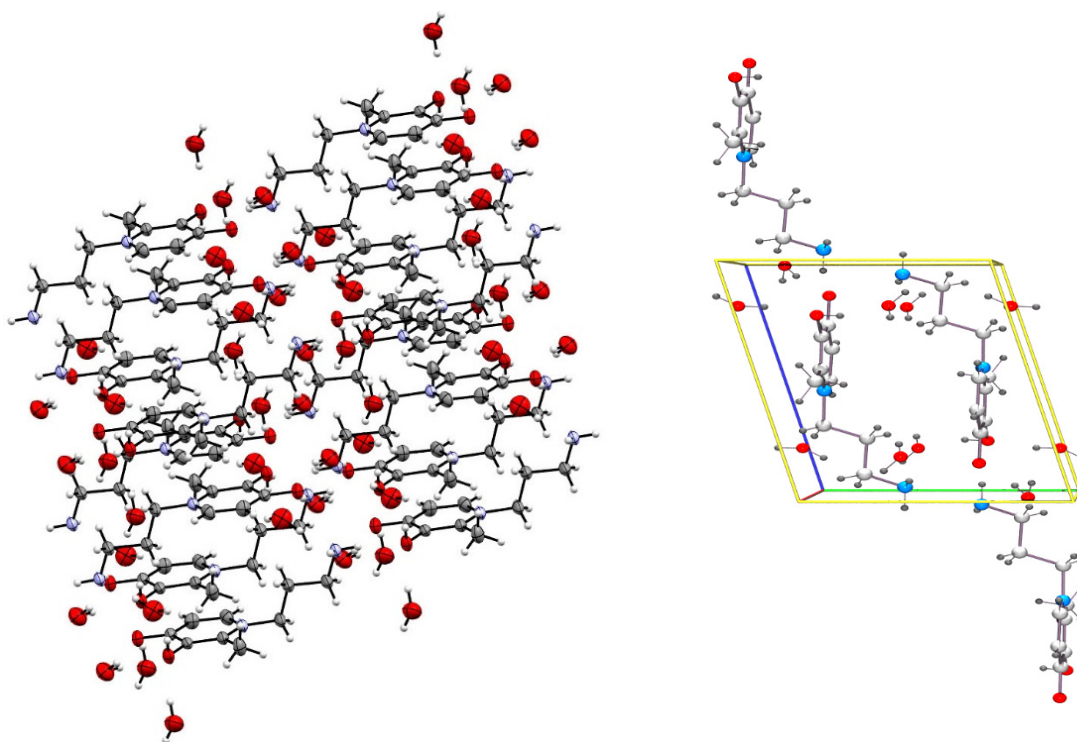


Figure S2. Packing diagram of H(L1) showing thermal displacement ellipsoids, drawn at the 50% probability level (left) and view normal to (100) plane (right).

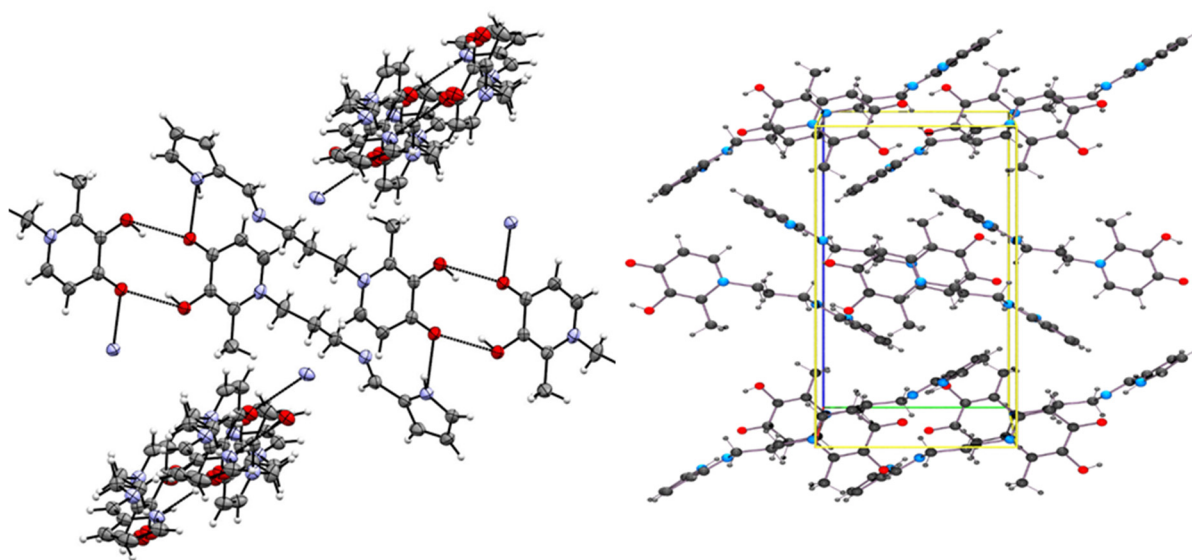


Figure S3. Packing diagram of H(L2) showing thermal displacement ellipsoids, drawn at the 50% probability level (left) and view normal to (100) plane (right).

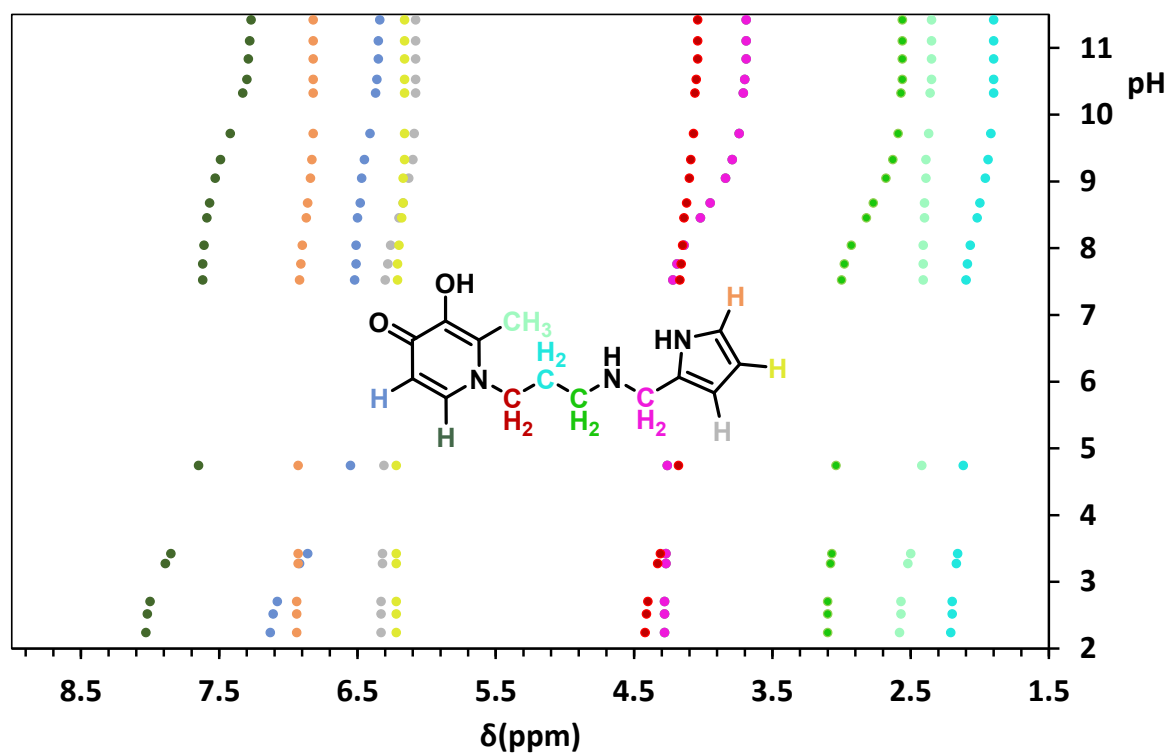


Figure S4. pH dependence of the chemical shifts of H(L3) in D_2O .

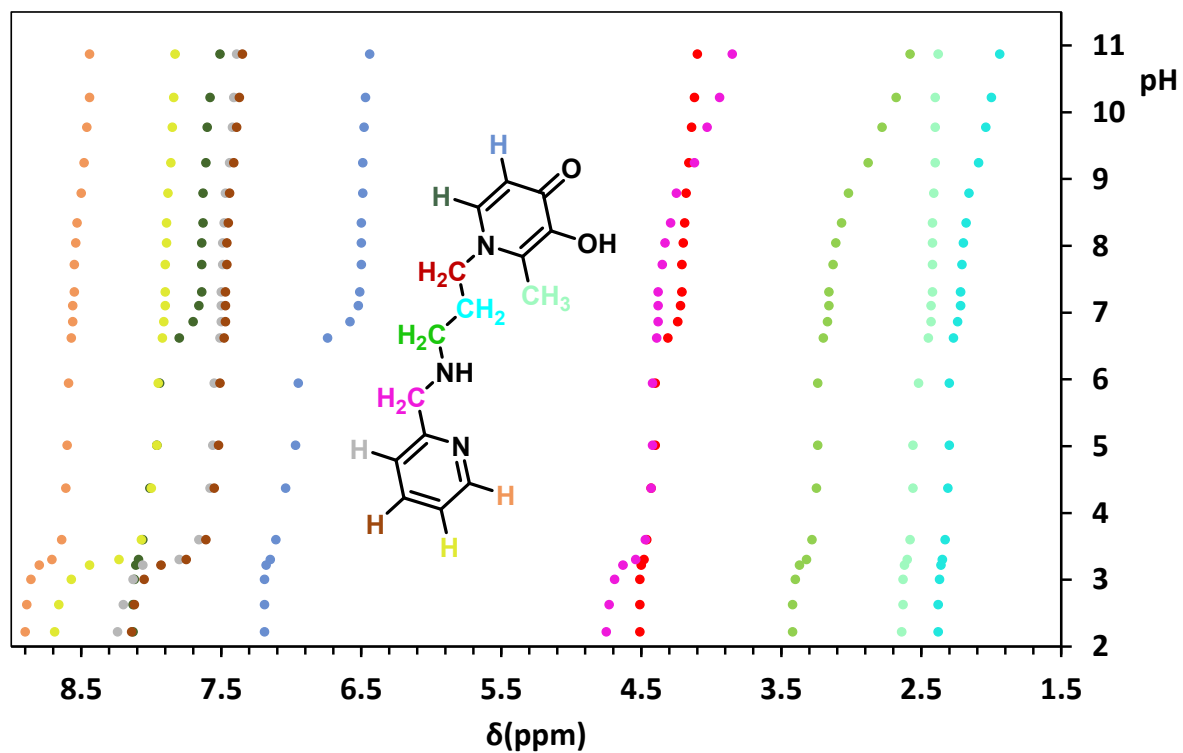


Figure S5. pH dependence of the chemical shifts of H(L5) in D₂O.

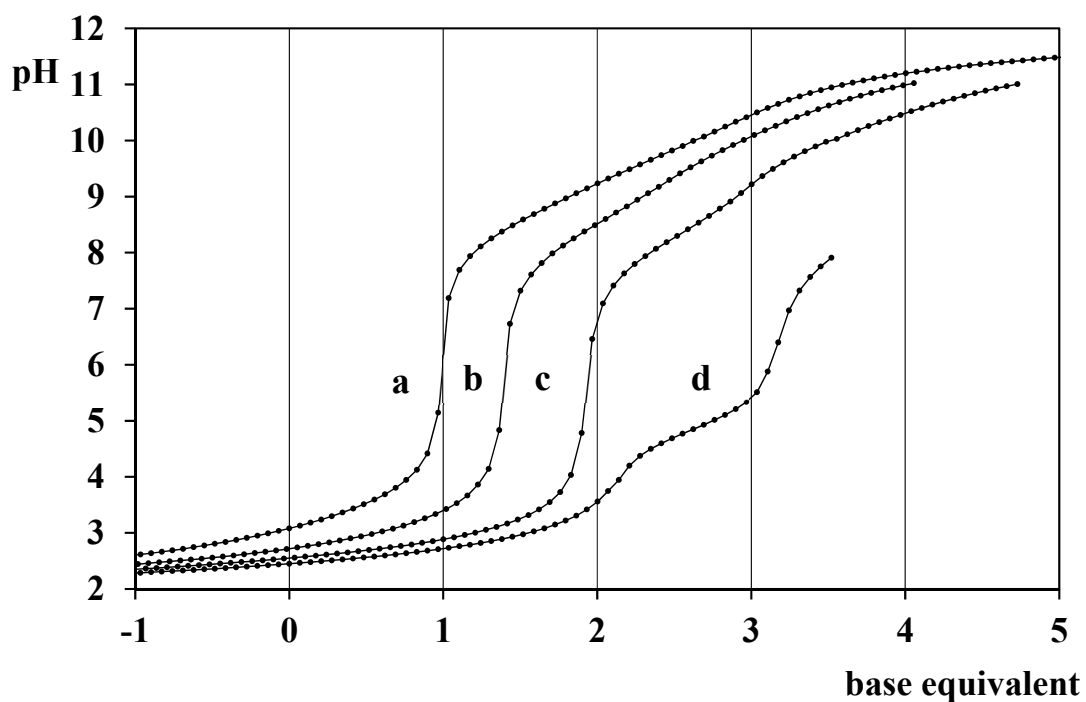


Figure S6. Representative titration curves of the H⁺–L3 (a) system and the [(η⁶-p-cym)Ru]²⁺–L3 system at 1:2 (b), 1:1 (c) and 2:1 (d) metal ion to ligand ratios (*c*_{L3} = 2.53 mM). Negative base equivalent refers to an excess of acid in the sample.

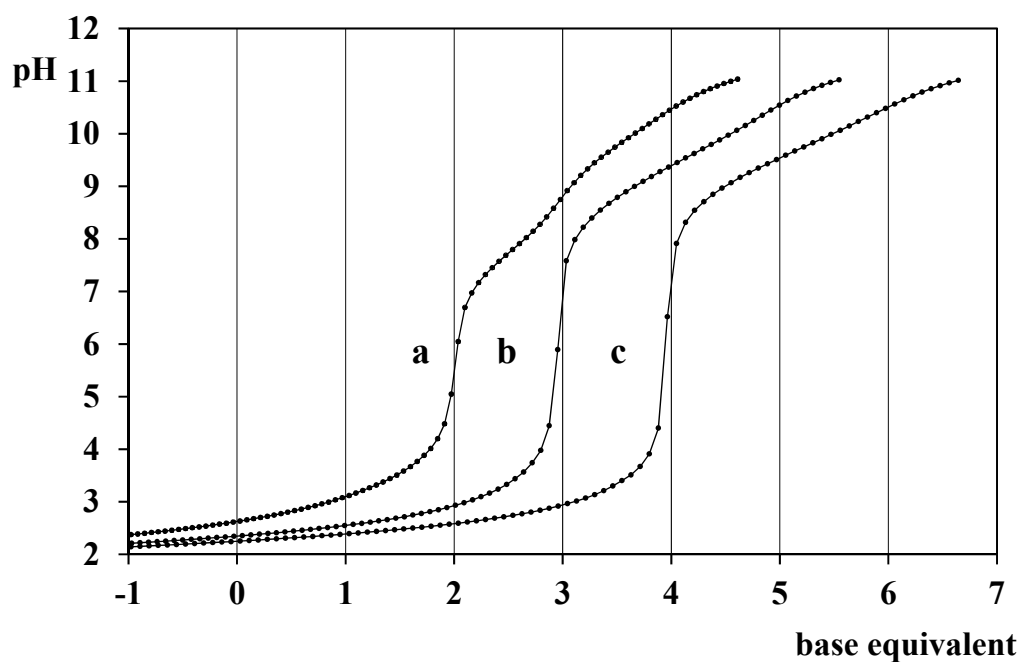


Figure S7. Representative titration curves of the H^+ –L5 (a) system and the $[(\eta^6\text{-}p\text{-cym})\text{Ru}]^{2+}$ –L5 system at 1:1 (b) and 2:1 (c) metal ion to ligand ratios ($c_{\text{L5}} = 2.60 \text{ mM}$). Negative base equivalent refers to an excess of acid in the sample.

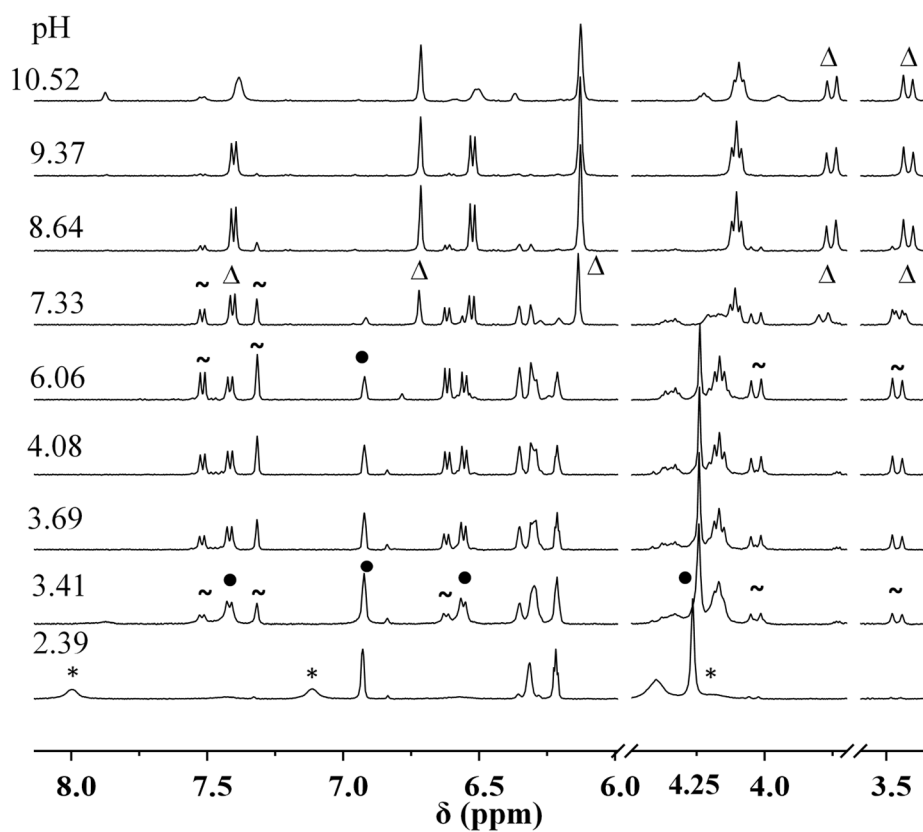


Figure S8. pH-dependence of the signals belonging to the L3 protons of a 2.3:1 $[(\eta^5\text{-Cp}^*)\text{Rh}]^{2+}$ -L3 sample, $c_{L3} = 5.0$ mM. Symbols represent the signals of the following species: $H_x(L3)$ (*), $[MHL]^{2+}$ (•), $[M_2L]^{3+}$ (~), $[M_2H_{-1}L]^{2+}$ (Δ).

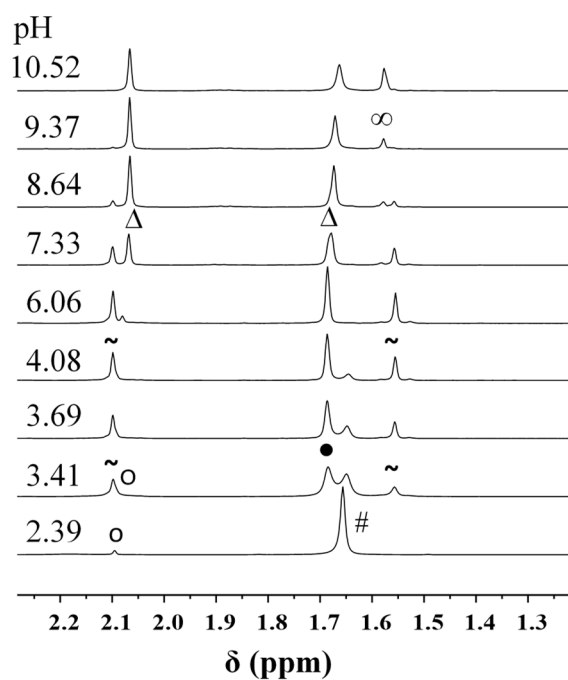


Figure S9. pH-dependence of the signals belonging to the Cp* CH₃ protons of a 2.3:1 [(η⁵-Cp*)Rh]²⁺-L3 sample, c_{L3} = 5.0 mM. Symbols represent the signals of the following species: H_x(L3) (*), [(η⁵-Cp*)Rh]²⁺ (#), (O,O) coordinated [MHL]²⁺ (•), (N,N) coordinated [MH₂L]³⁺ or [MHL]²⁺ (o), [M₂L]³⁺ (~), [M₂H₋₁L]²⁺ (Δ), [M₂(OH)₃]⁺ (∞).

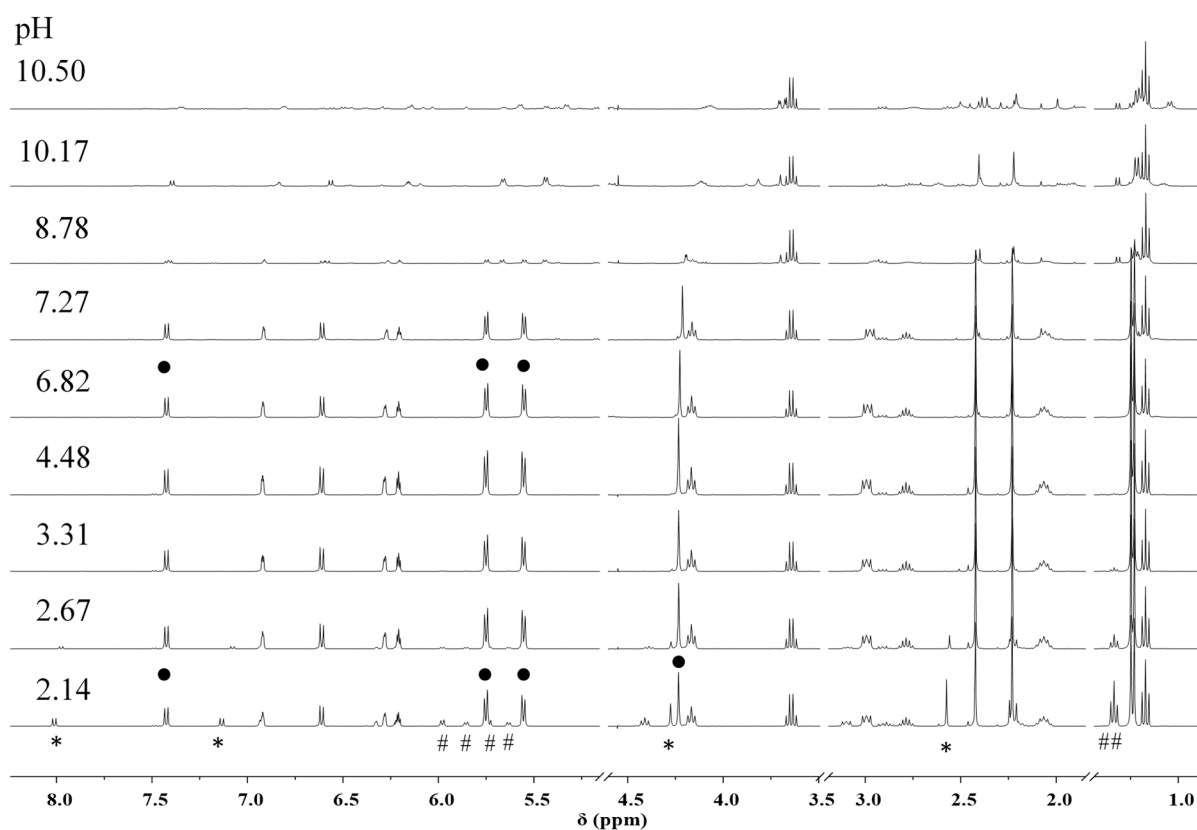


Figure S10. pH-dependence of the signals belonging to the protons in the $[(\eta^6\text{-}p\text{-cym})\text{Ru}]^{2+}$ –L3 system at 1:1 ratio, $c_{\text{L3}} = 5.0$ mM. Symbols represent the signals of the following species: $\text{H}_x(\text{L3})$ (*), $[\text{M}(\text{H}_2\text{O})_3]^{2+}$ and $[\text{M}(\text{Cl})_3]^-$ (#), $[\text{MHL}]^{2+}$ (•).

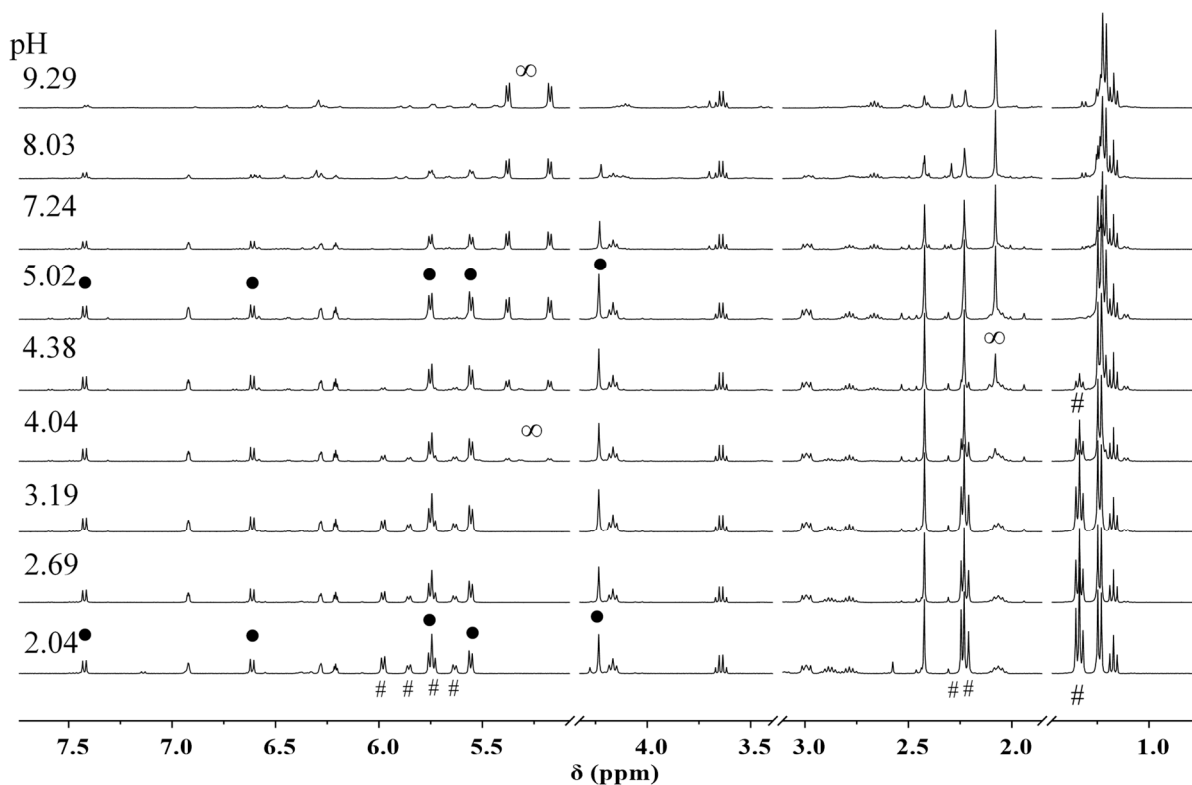


Figure S11. pH-dependence of the signals belonging to the protons in the $[(\eta^6\text{-}p\text{-cym})\text{Ru}]^{2+}$ –L3 system at 2:1 ratio, $c_{\text{L3}} = 5.0$ mM. Symbols represent the signals of the following species: $\text{H}_x(\text{L3})$ (*), $[\text{M}(\text{H}_2\text{O})_3]^{2+}$ and $[\text{M}(\text{Cl})_3]^-$ (#), $[\text{MHL}]^{2+}$ (•), $[\text{M}_2(\text{OH})_3]^+$ (∞).

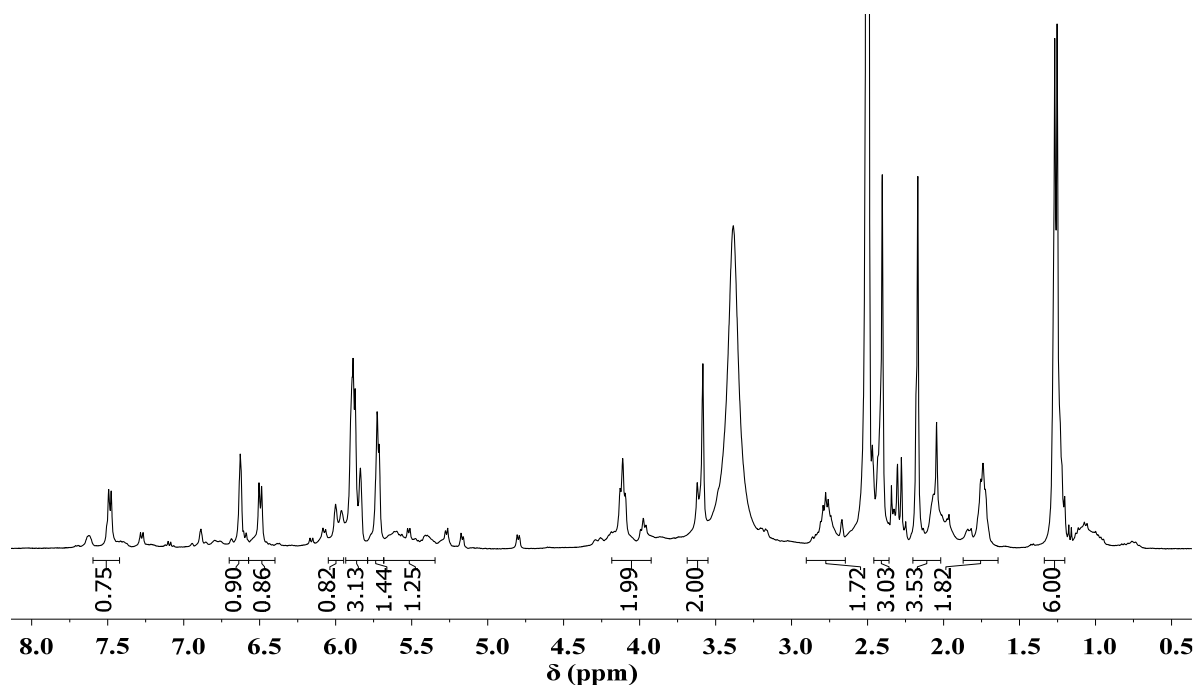


Figure S12. ^1H NMR spectrum of the precipitated yellow solid from a $[(\eta^6\text{-}p\text{-cym})\text{Ru}]^{2+}$ –L3 1:1 sample, pH ~ 8 , registered in d^6 -DMSO.

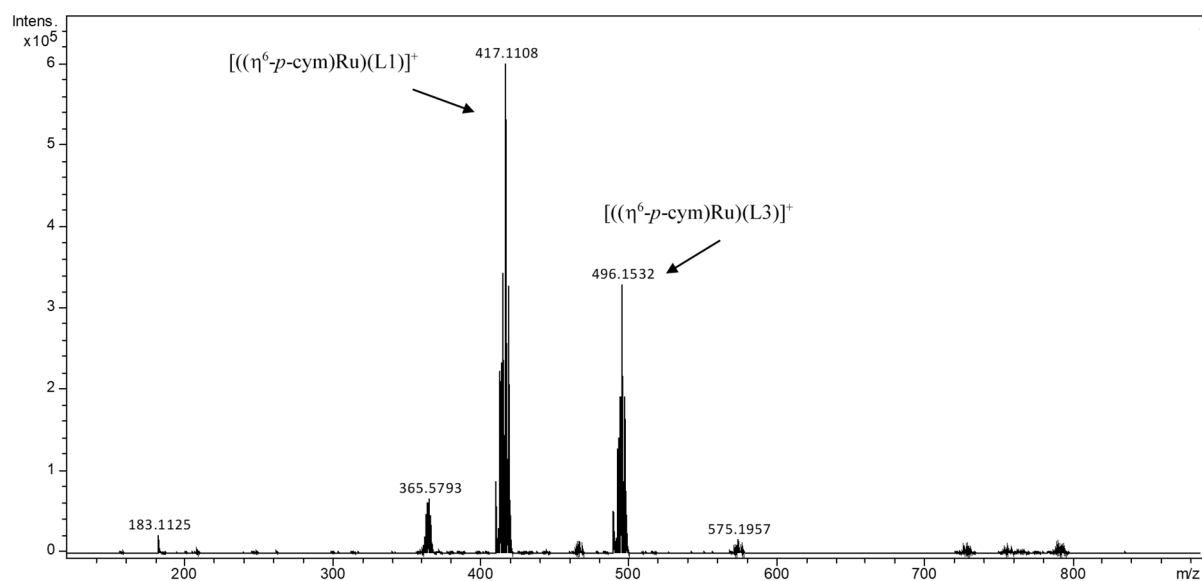


Figure S13. ESI-MS spectrum of the precipitated yellow solid from a $[(\eta^6\text{-}p\text{-cym})\text{Ru}]^{2+}$ -L3 1:1 sample.

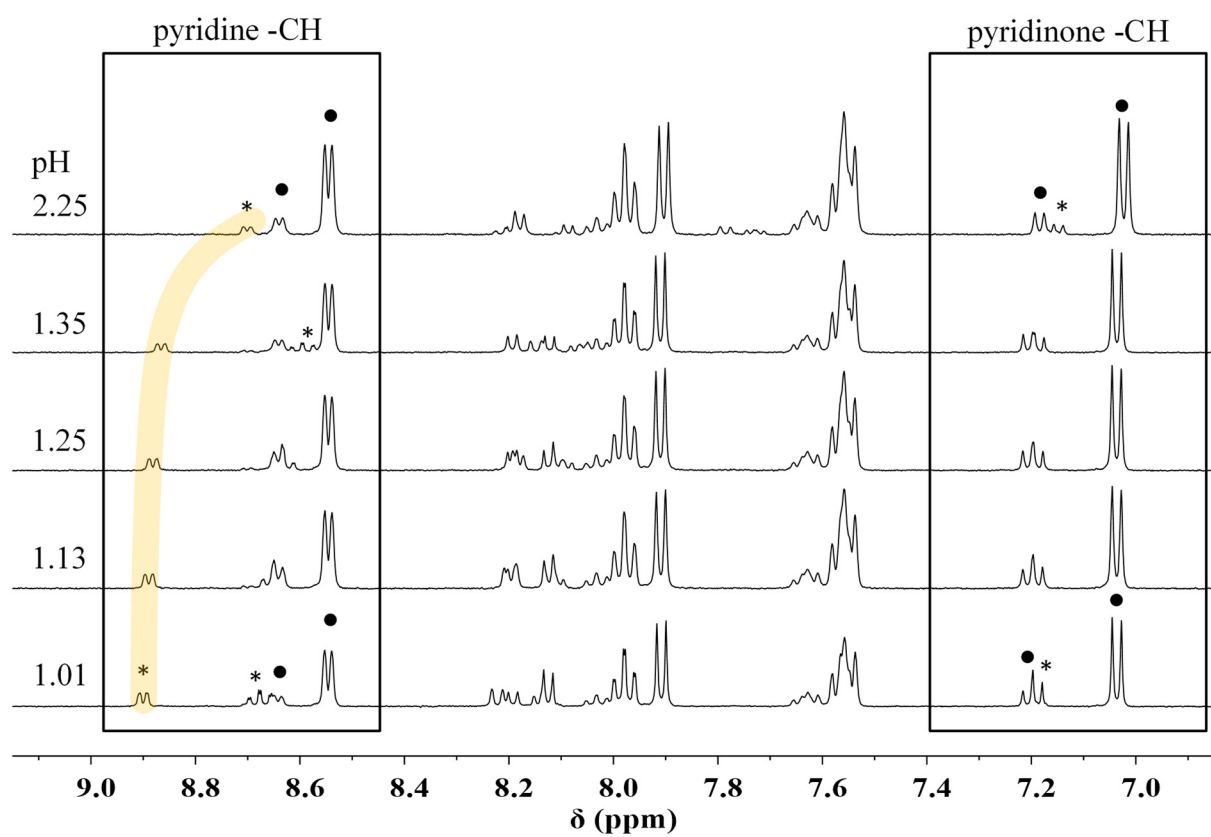


Figure S14. pH-dependence of the signals belonging to the L5 protons of a 1:1 $[(\eta^5\text{-Cp}^*)\text{Rh}]^{2+}$ –L5 sample, $c_{\text{L5}} = 5.0$ mM. Symbols represent the signals of the following species: $\text{H}_x(\text{L5})$ (*), $[\text{MH}_2\text{L}]^{3+}$ (•).

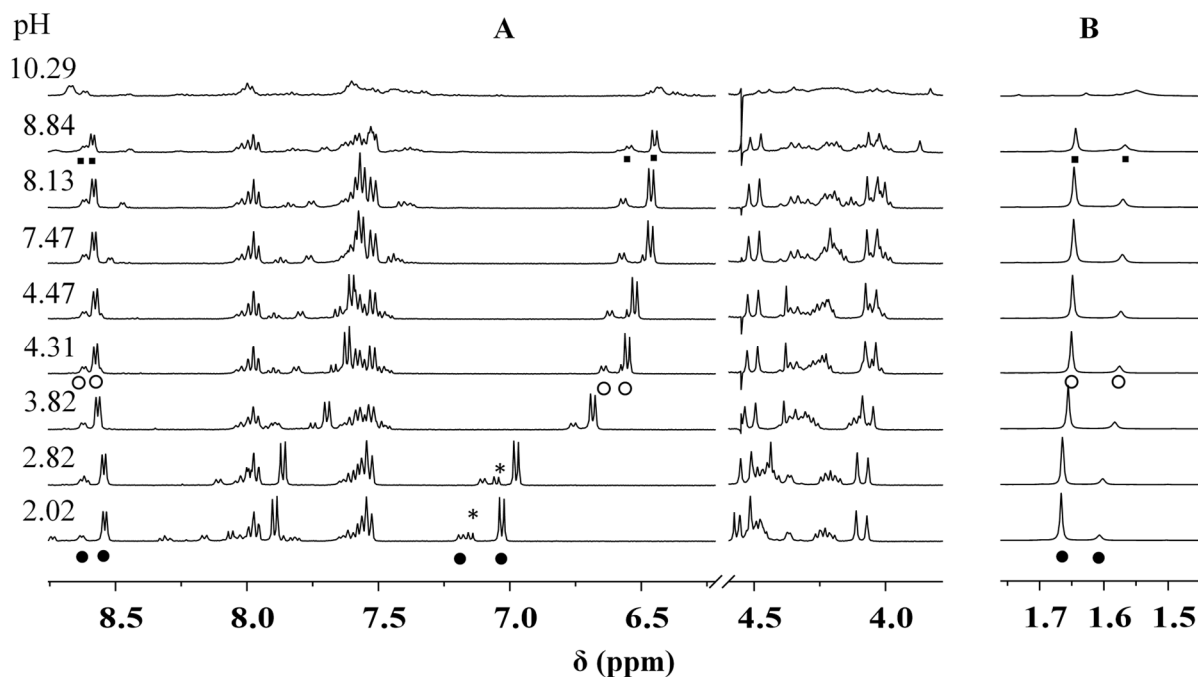


Figure S15. pH-dependence of the signals belonging to the L5 protons (A) and Cp* CH₃ protons (B) of a 0.93:1 $[(\eta^5\text{-Cp}^*)\text{Rh}]^{2+}$ -L5 sample, $c_{L5} = 5.0$ mM. Symbols represent the signals of the following species: $H_x(L5)$ (*), $[MH_2L]^{3+}$ (•), $[MHL]^{2+}$ (○), $[ML]^+$ (▪). The intensity scales are different for Figs. A and B for clarity.

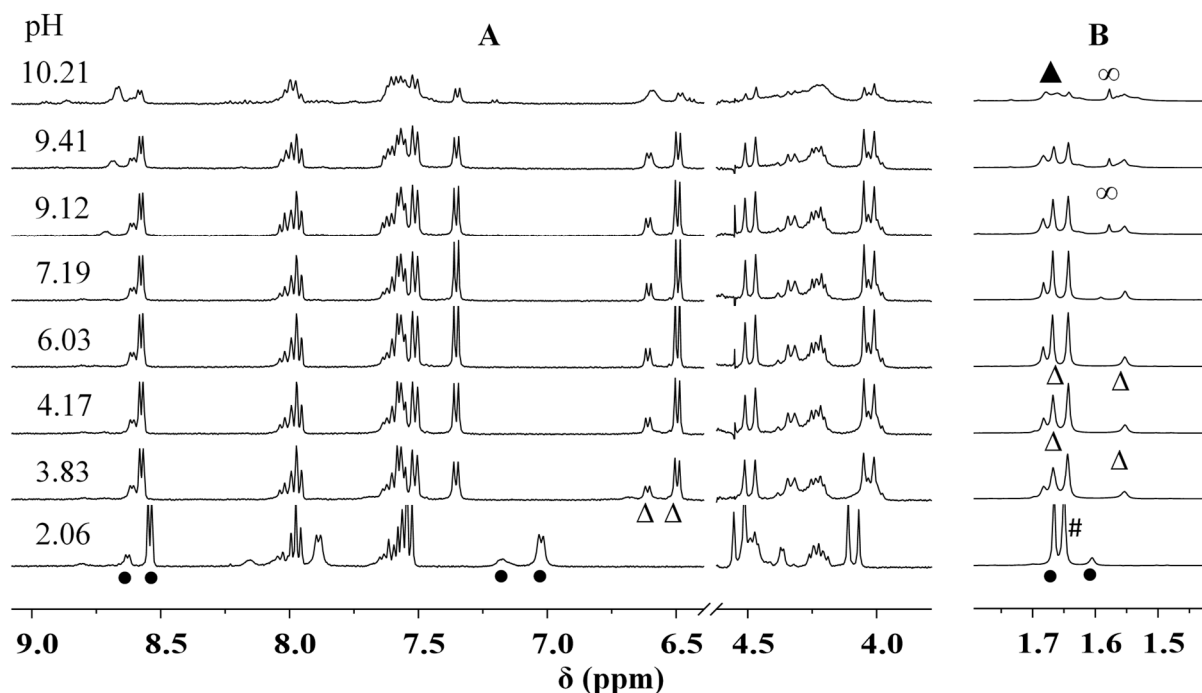


Figure S16. pH-dependence of the signals belonging to the L5 protons (A) and Cp* CH₃ protons (B) of a 2:1 $[(\eta^5\text{-Cp}^*)\text{Rh}]^{2+}$ -L5 sample, $c_{L5} = 5.0$ mM. Symbols represent the signals of the following species: $[M(H_2O)_3]^{2+}$ and $[M(Cl)_3]^-$ (#), $[MH_2L]^{3+}$ (•), $[M_2L]^{3+}$ (Δ), $[M_2H-1L]^{2+}$ (\blacktriangle), $[M_2(OH)_3]^+$ (∞).

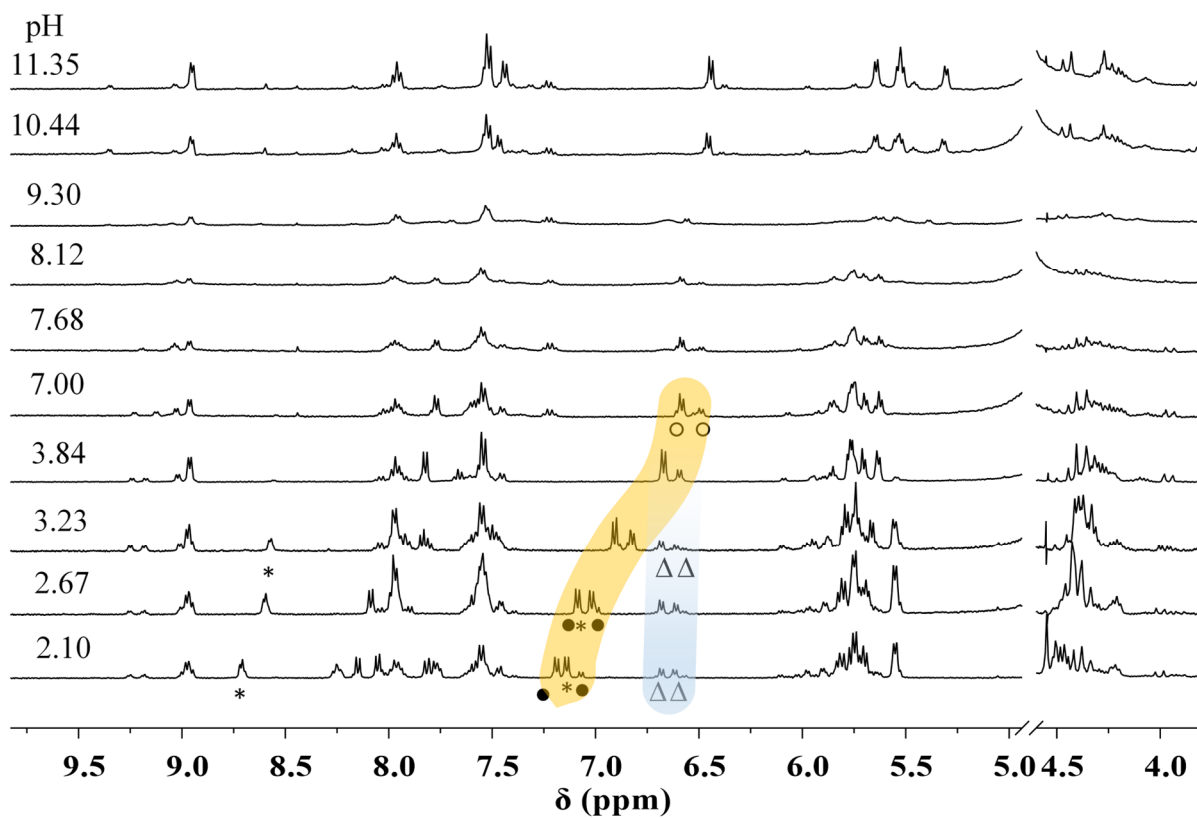


Figure S17. pH-dependence of the signals belonging to protons in the $[(\eta^6\text{-}p\text{-cym})\text{Ru}]^{2+}\text{-L5}$ system at 1:1 ratio, $c_{\text{L5}} = 5.0$ mM. Symbols represent the signals of the following species: $\text{H}_x(\text{L5})$ (*), $[\text{M}(\text{H}_2\text{O})_3]^{2+}$ and $[\text{M}(\text{Cl})_3]^-$ (#), $[\text{MH}_2\text{L}]^{3+}$ (•), $[\text{MHL}]^{2+}$ (○), $[\text{M}_2\text{L}]^{3+}$ (Δ), $[\text{M}_2(\text{OH})_3]^+$ (∞).

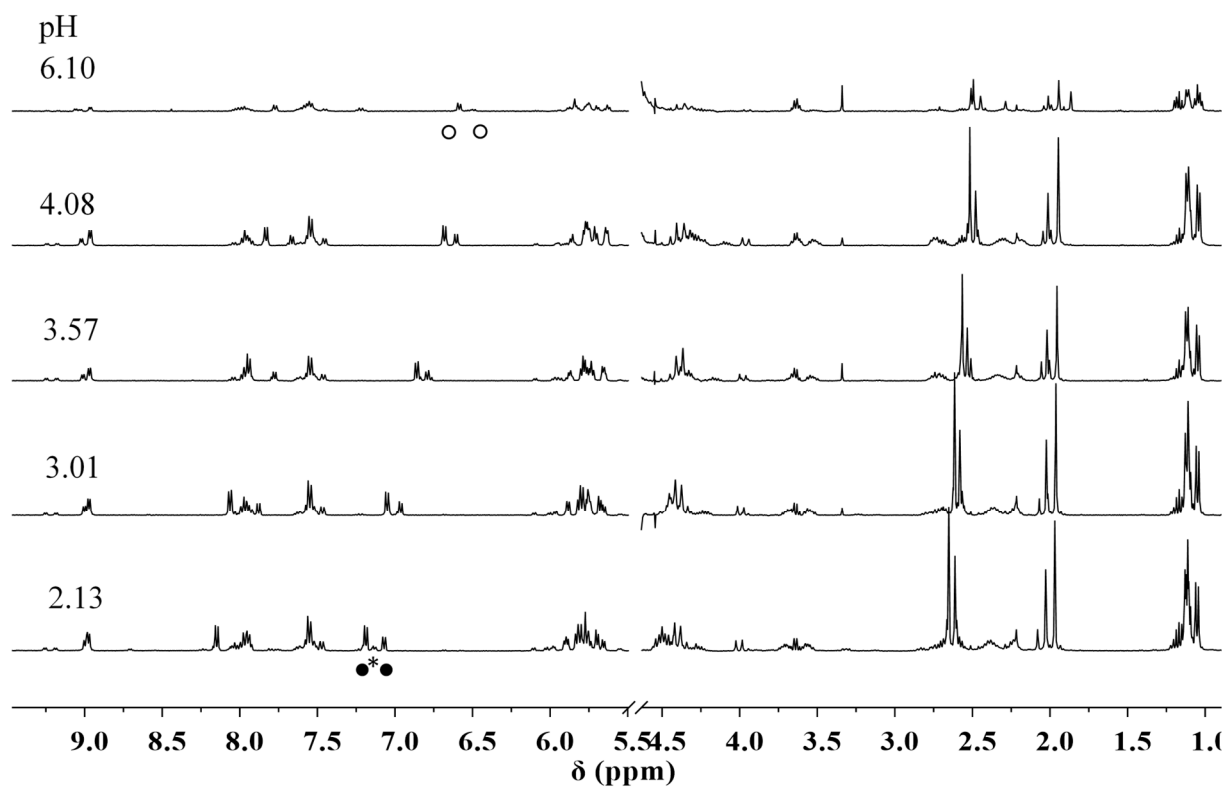


Figure S18. pH-dependence of the signals belonging to the protons in the $[\eta^6\text{-}p\text{-cym})\text{Ru}]^{2+}\text{-L5}$ system at 1:1 ratio, $c_{\text{L5}} = 5.0$ mM, $t = 48$ h. Symbols represent the signals of the following species: $\text{H}_x(\text{L5})$ (*), $[\text{M}(\text{H}_2\text{O})_3]^{2+}$ and $[\text{M}(\text{Cl})_3]^-$ (#), $[\text{MH}_2\text{L}]^{3+}$ (●), $[\text{MHL}]^{2+}$ (○).

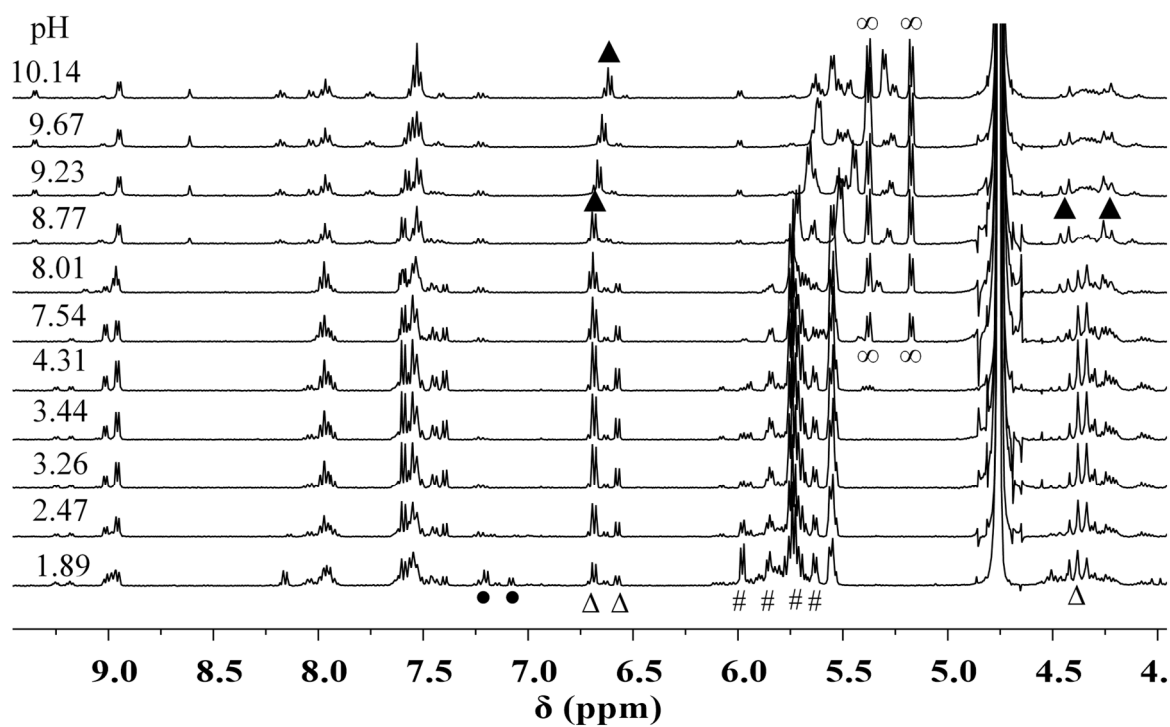


Figure S19. pH-dependence of the signals belonging to the protons in the $[(\eta^6\text{-}p\text{-cym})\text{Ru}]^{2+}$ –L5 system at 2.2:1 ratio, $c_{\text{L5}} = 5.0$ mM. Symbols represent the signals of the following species: $\text{H}_x(\text{L5})$ (*), $[\text{M}(\text{H}_2\text{O})_3]^{2+}$ and $[\text{M}(\text{Cl})_3]^-$ (#), $[\text{MH}_2\text{L}]^{3+}$ (•), $[\text{M}_2\text{L}]^{3+}$ (Δ), $[\text{M}_2\text{H-1L}]^{2+}$ (\blacktriangle), $[\text{M}_2(\text{OH})_3]^+$ (∞).

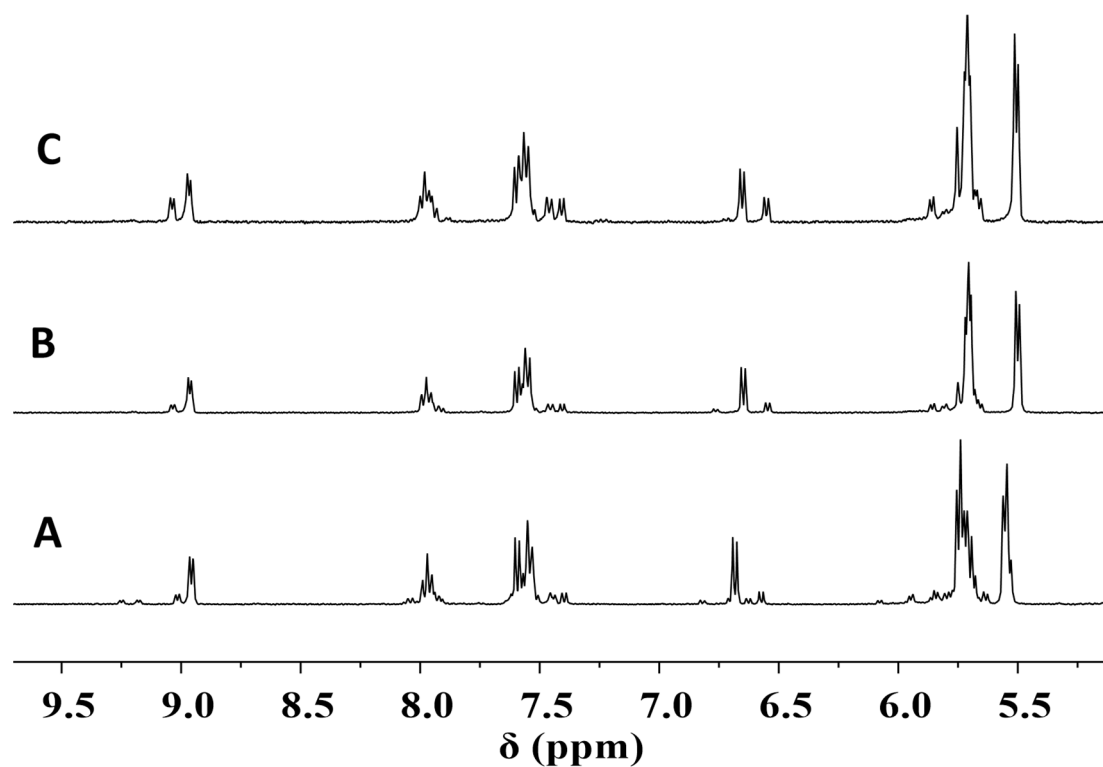


Figure S20. Dependence on time and chloride ion concentration of the low field NMR spectra registered in the $[(\eta^6\text{-}p\text{-cym})\text{Ru}]^{2+}\text{-L5}$ system at 2:1 metal ion to ligand ratio ($c_{\text{L5}} = 5 \text{ mM}$). A: $I = 0.20 \text{ M (KNO}_3)$; $\text{pH} = 3.74$; $t = 0 \text{ h}$. B: $I = 0.20 \text{ M (KNO}_3) + 0.20 \text{ M (KCl)}$; $\text{pH} = 3.74$; $t = 0 \text{ h}$. C: $I = 0.20 \text{ M (KNO}_3) + 0.20 \text{ M (KCl)}$; $\text{pH} = 3.74$; $t = 24 \text{ h}$.