

Electronic Supplementary Information (ESI) for

Dissolved N₂ sensing by pH-dependent Ru complexes

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Synthesis and Characterisation



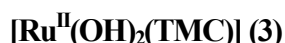
To an aqueous solution (5.0 mL) of $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{TMC})]\text{Cl}$ (120 mg, 259 μmol) was added AgNO_3 (223 mg, 1.31 mmol) under an Ar atmosphere and the suspension was stirred for 30 min. After precipitates were removed by filtration, Mg (125 mg, 5.14 mmol) was added to the filtrate and the suspension was stirred for 48 h. After precipitates were removed by filtration, the pH of the filtrate was adjusted to pH 2.0 by using 2.0 M $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$. To the resulting solution was added a saturated aqueous solution (2.6 mL) of KPF_6 (202 mg, 1.10 mmol). The precipitates were collected by filtration to obtain a product of $[\text{Ru}^{\text{II}}(\text{H}_2\text{O})_2(\text{TMC})](\text{PF}_6)_2$ $\{\mathbf{1}\}(\text{PF}_6)_2$ {yield: 11% based on $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{TMC})]\text{Cl}$ }.

Anal. Calcd for $[\mathbf{1}](\text{PF}_6)_2$: $\text{C}_{14}\text{H}_{36}\text{N}_4\text{F}_{12}\text{O}_2\text{P}_2\text{Ru}$: C, 24.60; H, 5.31; N, 8.20. Found: C, 24.64; H, 5.30; N, 8.49. FT-IR (cm^{-1} , as a KBr disk): 3415 (H_2O), 2930 (aliphatic C-H), 1640, 1472, 1300, 1140, 838 (PF_6), 760. UV-vis (in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ at pH 2.0 under an Ar atmosphere): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 230 (sh, 4200), 310 (sh, 360). ^1H NMR (in $\text{DNO}_3/\text{D}_2\text{O}$ at pD 3.0 under an Ar atmosphere): δ 2.75 (s, 12H, N- CH_3), 1.65-4.16 (m, 20H, - CH_2 -).



[Method A] Complex $[\mathbf{1}](\text{PF}_6)_2$ (2.4 mg, 3.5 μmol) was dissolved in water (3.0 mL) and the pH of the resulting solution was adjusted to pH 7.0 by using 10 mM $\text{NaOH}/\text{H}_2\text{O}$ under an Ar atmosphere. The water was evaporated to yield a yellow powder of $[\text{Ru}^{\text{II}}(\text{OH})(\text{H}_2\text{O})(\text{TMC})](\text{PF}_6)$ $\{\mathbf{2}\}(\text{PF}_6)$. The powder was collected and dried in vacuo {yield: 98% based on $[\mathbf{1}](\text{PF}_6)_2$ }. **[Method B]** Complex $[\mathbf{4}](\text{PF}_6)$ (11.0 mg, 19.5 μmol) was dissolved in water (1.0 mL) and the pH of the resulting solution was adjusted to pH 3.0 by using 2.0 M $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ under an Ar atmosphere. Ar was bubbled through the solution for 1 h. The pH of the solution was adjusted to pH 6.5 by using 4.0 M $\text{NaOH}/\text{H}_2\text{O}$. The solution was concentrated to give a yellow powder of $[\mathbf{2}](\text{PF}_6)$. The powder was collected and dried in vacuo {yield: 95% based on $[\mathbf{4}](\text{PF}_6)$ }.

Anal. Calcd for $[\mathbf{2}](\text{PF}_6) \cdot 0.5\text{Na}_2\text{SO}_4$: $\text{C}_{14}\text{H}_{35}\text{N}_4\text{F}_6\text{NaO}_4\text{PRuS}_{0.5}$: C, 27.63; H, 5.80; N, 9.21; S, 2.63. Found: C, 27.91; H, 5.80; N, 9.35; S, 2.90. It was confirmed by IR that the sample for the elemental analysis included Na_2SO_4 , which could be derived from $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ and $\text{NaOH}/\text{H}_2\text{O}$. ESI-MS (in CH_3OH): m/z 375.1 $\{[\mathbf{2} - \text{H}_2\text{O}]^+\}$; relative intensity (I) = 100% in the range of m/z 100-2000}. FT-IR (cm^{-1} , as a KBr disk): 3700 (O-H), 3450 (H_2O), 2930 (aliphatic C-H), 1637, 1473, 1135, 1117 (SO_4), 836 (PF_6). UV-vis (in H_2O at pH 7.0 under an Ar atmosphere): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 230 (sh, 4000), 309 (720). ^1H NMR (in D_2O at pD 7.0 under an Ar atmosphere): δ 2.71 (s, 12H, N- CH_3), 1.66-3.82 (m, 20H, - CH_2 -).



To an aqueous solution (2.0 mL) of $[\mathbf{2}](\text{PF}_6)$ (2.3 mg, 4.3 μmol) was added 1.0 M $\text{NaOH}/\text{H}_2\text{O}$ over pH 11.2 under an Ar atmosphere and the solvent of water was evaporated. To the residue was added acetone (1.0 mL) and insoluble solids were removed by filtration. The solvent of the filtrate was evaporated to yield an air-sensitive powder of $[\text{Ru}^{\text{II}}(\text{OH})_2(\text{TMC})]$ ($\mathbf{3}$). The powder was

collected and dried in vacuo {yield: 43% based on [2](PF₆)}.

Anal. Calcd for 3•NaPF₆•(CH₃)₂CO: C₁₇H₄₀N₄F₆NaO₃PRu: C, 33.06; H, 6.53; N, 9.07. Found: C, 32.74; H, 5.60; N, 9.36. It was confirmed by IR that the sample for the elemental analysis included NaPF₆. FT-IR (cm⁻¹, as a KBr disk): 3630 (O-H), 2920 (aliphatic C-H), 1637, 1470, 842 (PF₆). UV-vis (in NaOH/H₂O at pH 11.2 under an Ar atmosphere): λ_{max}/nm (ε/M⁻¹ cm⁻¹): 230 (sh, 3500). ¹H NMR (in NaOD/D₂O at pD 11.2 under an Ar atmosphere): δ 2.72 (s, 12H, N-CH₃), 1.67-4.12 (m, 20H, -CH₂-).

[Ru^{II}(OH)(TMC)(N₂)](PF₆) {4}(PF₆)

[Method A] Complex [2](PF₆) (48.0 mg, 89.3 μmol) was added to 1.0 mM NaOH/H₂O (3.0 mL) under an Ar atmosphere. N₂ gas was bubbled through the resulting solution at 25 °C for 10 min. The solvent of water was evaporated to yield a yellow powder of [Ru^{II}(OH)(TMC)(N₂)](PF₆) {4}(PF₆). The powder was collected and dried in vacuo {yield: 98% based on [2](PF₆)}.

[Method B] To an aqueous solution (5.0 mL) of [Ru^{III}Cl₂(TMC)]Cl (722 mg, 1.56 mmol) was added Mg (300 mg, 12.3 mmol) under a N₂ atmosphere and the suspension was stirred for 18 h. After filtration, 1.0 M NaOH/H₂O (50 μL) was added to the filtrate and the resulting solution was stirred for 18 h. After precipitates were removed by filtration, a saturated aqueous solution (2.7 mL) of KPF₆ (200 mg, 1.09 mmol) was added to the filtrate. The water was removed by evaporation. The residue was dissolved in dichloromethane (3.0 mL) and insoluble solids were filtered off. Recrystallisation of the filtrate with diethyl ether (3.0 mL) gave pale yellow needle crystals of [4](PF₆) {yield: 61% based on [Ru^{III}Cl₂(TMC)]Cl}.

Anal. Calcd for [4](PF₆)•0.5CH₂Cl₂: C_{14.5}H₃₄N₆ClF₆PRu: C, 29.52; H, 5.81; N, 14.25. Found: C, 29.27; H, 5.85; N, 14.12. ESI-MS (in CH₃OH): *m/z* 403.2 {[4]⁺; *I* = 100% in the range of *m/z* 100-2000}, 375.2 {[4 - N₂]⁺; *I* = 66% in the range of *m/z* 100-2000}. FT-IR (cm⁻¹, as a KBr disk): 3640 (O-H), 2900 (aliphatic C-H), 2050 (N≡N), 1467, 993, 840 (PF₆). UV-vis (in NaOH/H₂O at pH 11.2 under a N₂ atmosphere): λ_{max}/nm (ε/M⁻¹ cm⁻¹): 235 (12500), 310 (sh, 1000). ¹H NMR (in NaOD/D₂O at pD 11.2 under a N₂ atmosphere): δ 2.76 (s, 12H, N-CH₃), 1.68-4.14 (m, 20H, -CH₂-).

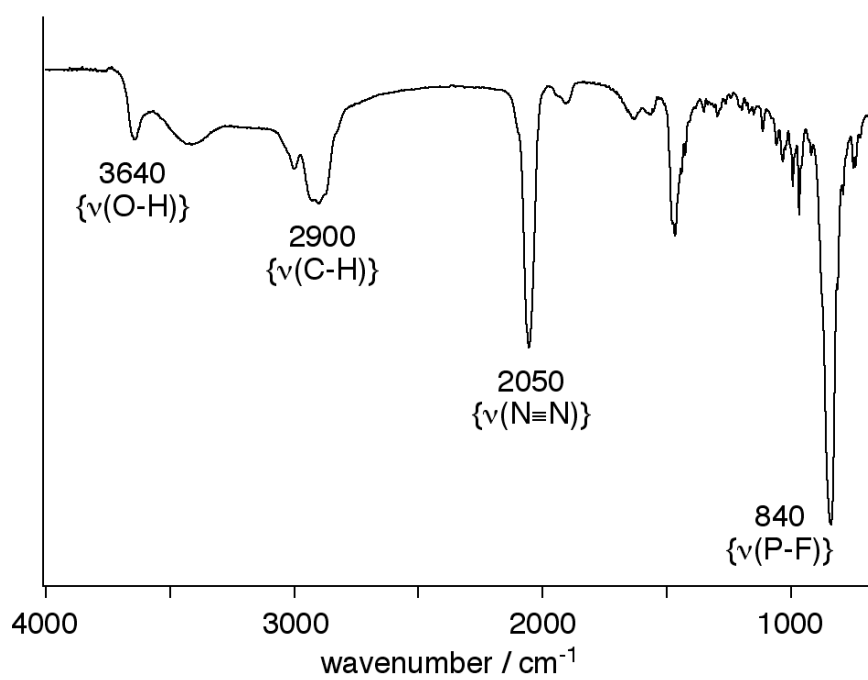


Fig. S1 IR spectrum of [4](PF₆) as a KBr disk.

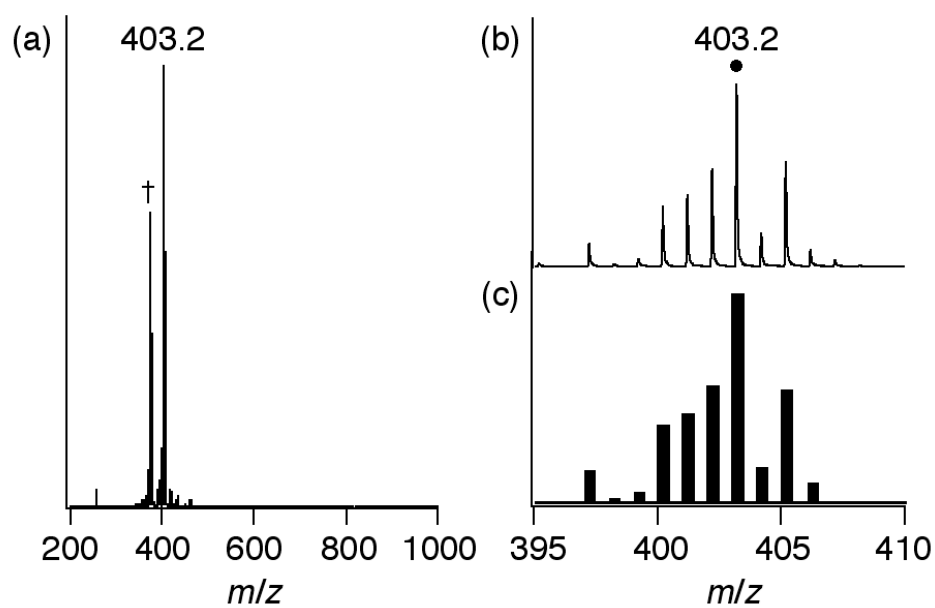


Fig. S2 (a) Positive-ion ESI mass spectrum of [4](PF₆) in methanol. The signal denoted with a dagger at *m/z* 375.2 corresponds to [4 - N₂]⁺. (b) The signal at *m/z* 403.2 corresponds to [4]⁺. (c) Calculated isotopic distribution for [4]⁺.

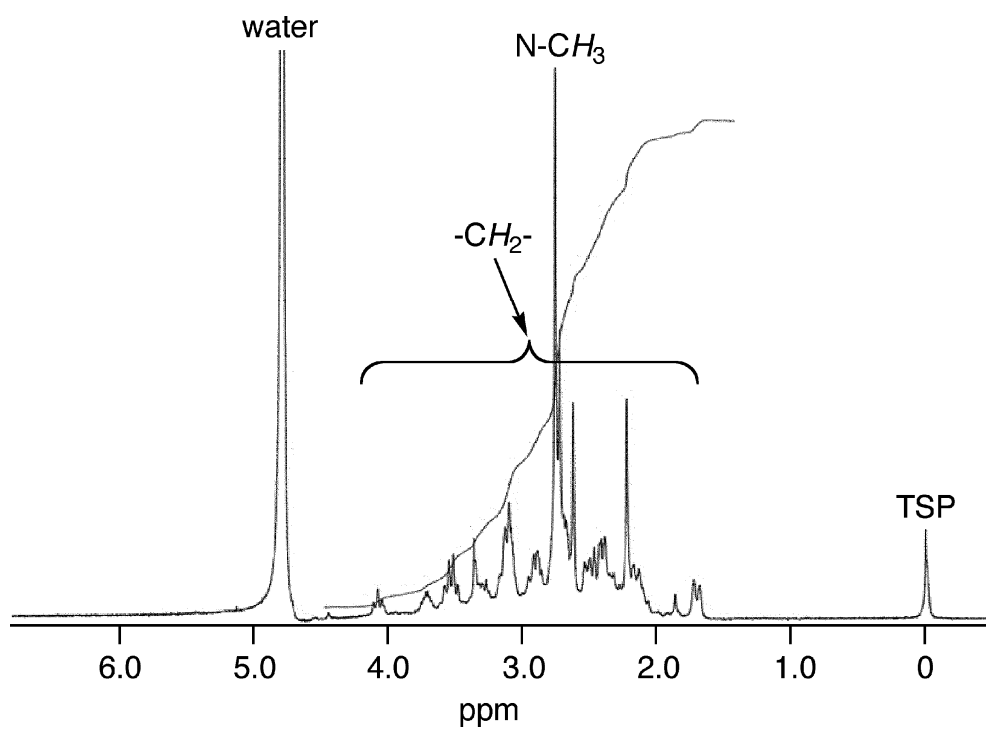


Fig. S3 ^1H NMR spectrum of [4](PF₆) in NaOD/D₂O at pD 11.2 at 25 °C under a N₂ atmosphere. TSP: the reference with methyl proton resonance set at 0.00 ppm.