

Electronic Supplementary Information

for

**Novel Synthesis of a Four-Electron-Reduced Ruthenium(II) NADH-Type Complex  
under Water-Gas-Shift Reaction Conditions**

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## Experimental

**Materials.** All chemicals used for the synthesis of the ligands and complexes were commercial products of the highest available purity and were further purified by the standard methods.<sup>1</sup> Solvents were also purified by standard methods before use.<sup>1</sup>

**Syntheses.** All ligands and complexes used in this study were prepared according to the following procedures and the structures of the products were confirmed by the analytical data (*vide infra*).

**2,2'-(4-(*tert*-butyl)pyridine-2,6-diyl)bis(benzo[*b*][1,5]naphthyridine (bbnp).** This ligand used in this study was synthesised in accordance with the method of the literature.<sup>2</sup>

**[Ru(bbnpH<sub>4</sub>)(CO)<sub>2</sub>Cl](PF<sub>6</sub>) (1•H<sub>4</sub>) synthesized by using bbnp and [Ru(CO)<sub>2</sub>Cl<sub>2</sub>].** In a 100 mL autoclave vessel, NAD<sup>+</sup>-type bbnp ligand (52 mg, 0.11 mmol) and [Ru(CO)<sub>2</sub>Cl<sub>2</sub>] (25 mg, 0.11 mmol) was mixed in 10 mL of 2-methoxyethanol/water (9:1 v/v) solvent. The autoclave was charged with 2.0 MPa CO, and the resulting mixture was stirred for 24 h at 140°C. After cooling the mixture to room temperature, **1•H<sub>4</sub>** was precipitated by addition of 10 mL aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (179 mg, 1.1 mmol), which was collected by filtration, washed with water, and dried in vacuo in good isolated yield (81 mg, 93%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 8.13 (2H, d, *J* = 8.8 Hz), 8.02 (2H, s), 7.90 (2H, s), 7.29 (2H, d, *J* = 8.7 Hz), 7.25 (2H, d, *J* = 7.6 Hz), 7.19 (2H, dt, *J* = 7.8, 1.3 Hz), 7.00 (2H, dt, *J* = 7.5, 1.2 Hz), 6.83 (2H, dt, *J* = 7.8, 0.8 Hz), 4.80 (2H, d, *J* = 20 Hz), 4.70 (2H, d, *J* = 20 Hz), 1.49 (9H, s) ppm. Anal. Calcd for C<sub>39.5</sub>F<sub>6</sub>H<sub>40.5</sub>N<sub>6.5</sub>O<sub>4</sub>PClRu: C, 49.85%; H, 4.29%; N, 9.57%; Found: C, 50.03%; H, 4.21%; N, 9.50%. ESI-TOF-MS: *m/z* = 688 [*M*-PF<sub>6</sub>]<sup>+</sup>.

**[Ru(bbnp)(CO)<sub>2</sub>Cl](PF<sub>6</sub>) (1).** A mixture of **1•H<sub>4</sub>** (51 mg, 0.061 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (56 mg, 0.25 mmol) in acetonitrile (15 mL) was stirred for 2 h at room temperature. An aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (104 mg, 0.64 mmol, 10 mL) was added to the mixture to precipitate a brown powder of **1**, which was collected by filtration, washed with water, and dried in vacuo (39 mg, 77%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 9.66 (2H, s), 9.12 (2H, d, *J* = 9.2 Hz), 9.03 (2H, d, *J* = 9.2 Hz), 8.87 (2H, s), 8.52 (2H, d, *J* = 8.5 Hz), 8.39 (2H, d, *J* = 8.6 Hz), 8.15 (2H, dt, *J* = 7.7, 1.3 Hz), 7.97 (2H, dt, *J* = 7.6, 0.9 Hz), 1.67 (9H, s) ppm. Anal. Calcd for C<sub>35</sub>F<sub>6</sub>H<sub>25</sub>N<sub>5</sub>O<sub>2</sub>PClRu: C, 50.70%; H, 3.04%; N, 8.45%; Found: C, 50.62%; H, 3.25%; N, 8.54%. ESI-TOF-MS: *m/z* = 684 [*M*-PF<sub>6</sub>]<sup>+</sup>.

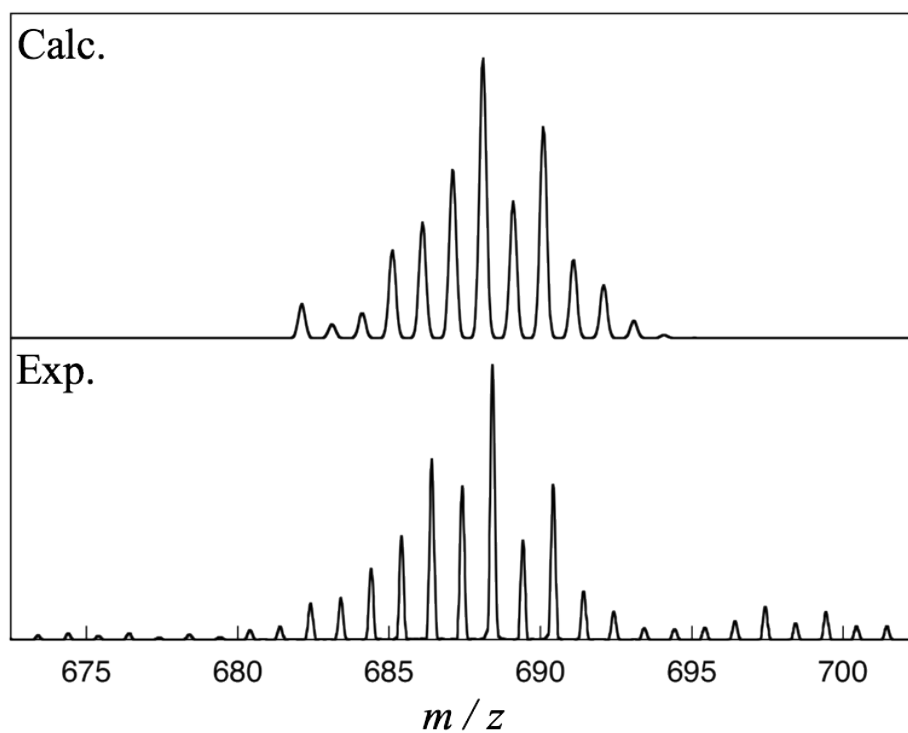
**[Ru(bbnpH<sub>4</sub>)(CO)<sub>2</sub>Cl](PF<sub>6</sub>) (1•H<sub>4</sub>) synthesized by using [Ru(bbnp)(CO)<sub>2</sub>Cl](PF<sub>6</sub>) (1).** In a 100 mL autoclave vessel, [Ru(bbnp)(CO)<sub>2</sub>Cl](PF<sub>6</sub>) (**1**) (10 mg, 0.012 mmol) was mixed in 10 mL of 2-methoxyethanol/water (9:1 v/v) solvent. The autoclave was charged with 2.0 MPa CO, and the resulting

mixture was stirred for 24 h at 140°C. After cooling the mixture to room temperature, **1•H<sub>4</sub>** was precipitated by addition of 10 mL aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (20 mg, 0.12 mmol), which was collected by filtration, washed with water, and dried in vacuo (7.8 mg, 78%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 8.13 (2H, d, *J* = 8.8 Hz), 8.02 (2H, s), 7.90 (2H, s), 7.29 (2H, d, *J* = 8.7 Hz), 7.25 (2H, d, *J* = 7.6 Hz), 7.19 (2H, dt, *J* = 7.8, 1.3 Hz), 7.00 (2H, dt, *J* = 7.5, 1.2 Hz), 6.83 (2H, dt, *J* = 7.8, 0.8 Hz), 4.80 (2H, d, *J* = 20 Hz), 4.70 (2H, d, *J* = 20 Hz), 1.49 (9H, s) ppm. ESI-TOF-MS: *m/z* = 688 [*M*-PF<sub>6</sub>]<sup>+</sup>.

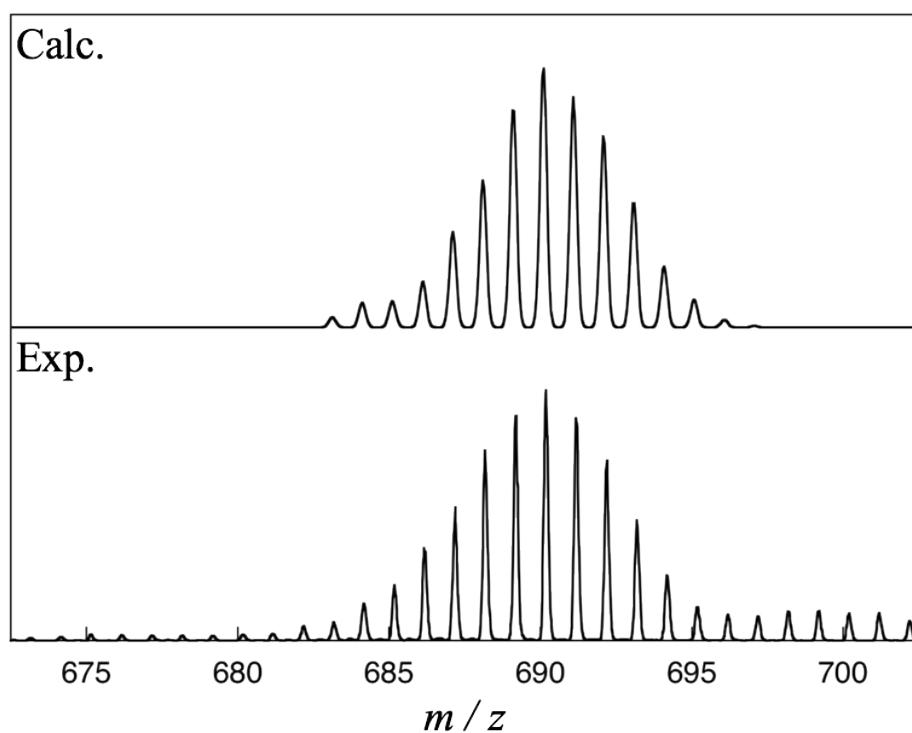
**Physical measurements.** NMR measurements were performed with a JEOL ECS-400 (400 MHz) NMR spectrometer. ESI-TOF mass spectra were obtained on a JEOL JMS-T100LP mass spectrometer. GC experiments were taken on a Shimadzu GC-14B gas chromatograph (Ar carrier) equipped with a thermal conductivity detector (TCD). Cyclic voltammetry measurements were performed on an ALS/Chi model 660A electrochemical analyzer in deaerated solvent containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as a supporting electrolyte. A conventional three-electrode cell was used with a glassy-carbon working electrode and a platinum wire as the counter electrode. The glassy-carbon working electrode was routinely polished with a BAS polishing alumina suspension and rinsed with acetone before use. All potentials were recorded against a Ag/Ag<sup>+</sup> reference electrode which was calibrated using an SCE reference. All electrochemical measurements were carried out under an atmospheric pressure of argon. The reaction experiments using D<sub>2</sub>O instead of H<sub>2</sub>O under WGS conditions to give [Ru(bbnPD<sub>2</sub>H<sub>2</sub>)(CO)<sub>2</sub>Cl]<sup>+</sup> (**1•D<sub>2</sub>H<sub>2</sub>**) (bbnPD<sub>2</sub>H<sub>2</sub> is the dideuterated analogue of bbnPH<sub>4</sub>) were conducted as follows: In a 100 mL autoclave vessel, NAD<sup>+</sup>-type bbnP ligand (77 mg, 0.16 mmol) and [Ru(CO)<sub>2</sub>Cl<sub>2</sub>] (37 mg, 0.16 mmol) was mixed in 10 mL of 2-methoxyethanol/deuterated water (9:1 v/v) solvent. The autoclave was charged with 2.0 MPa CO, and the resulting mixture was stirred for 24 h at 140°C. After cooling the mixture to room temperature, the resulting solutions were diluted with acetonitrile and then used to measure ESI-TOF mass spectra.

**X-ray crystal structure determination.** Well-shaped single crystals of **1•H<sub>4</sub>•2DMF**, which are suitable for X-ray crystallographic analysis, were grown by slow vapour diffusion of diethylether into a dimethylformamide (DMF) solution of **1•H<sub>4</sub>**. Data for **1•H<sub>4</sub>•2DMF** were collected on a Rigaku/MS Saturn CCD diffractometer using graphite-monochromated Mo-*K*α radiation ( $\lambda = 0.71075 \text{ \AA}$ ) at 123 K and processed using Crystal Clear program (Rigaku). The structure was solved by direct methods using SIR-2008<sup>3</sup> and refined by full-matrix least-squares techniques on *F*<sup>2</sup> using SHELXL-2016/4<sup>4</sup>. The absorption

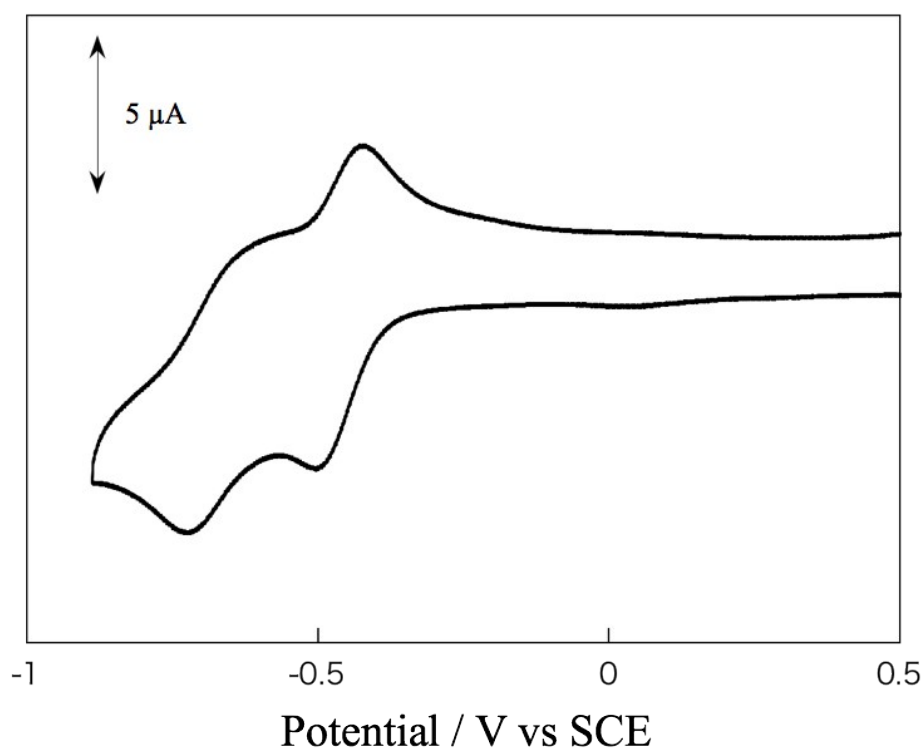
corrections were done using the multi-scan technique. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included in the refinement process as per the riding model.



**Fig. S1** Calculated (top) and observed (bottom) ESI-TOF mass spectra of **1•H<sub>4</sub>** generated by taking advantage of the water-gas-shift reaction (CO pressure: 2.0 MPa, temperature: 140°C, solvent: 2-methoxyethanol/water (9:1 v/v)) of **1** in CH<sub>3</sub>CN at 298 K.



**Fig. S2** Calculated (top) and observed (bottom) ESI-TOF mass spectra of the solution after the reaction using bbnp and  $[\text{Ru}(\text{CO})_2\text{Cl}_2]$  under the water-gas-shift reaction conditions (CO pressure: 2.0 MPa, temperature: 140°C, solvent: 2-methoxyethanol/deuterated water (9:1 v/v)) in  $\text{CH}_3\text{CN}$  at 298 K.<sup>5</sup>



**Fig. S3** Cyclic voltammogram of **1** in propylene carbonate (1.0 mM) containing 0.1 M TBAPF<sub>6</sub> at 298 K (working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, Ag/Ag<sup>+</sup>; scan rate, 100 mV s<sup>-1</sup>).

## Notes and References

- 1 W.L.F. Armarego, C.L.L. Chai, in *Purification of laboratory chemicals, 6th ed.*, Pergamon Press, Oxford, U.K., **2009**.
- 2 H. Tannai, T-a. Koizumi, K. Tanaka, *Inorg. Chim. Acta* **2007**, *360*, 3075.
- 3 M. C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna, *J. Appl. Cryst.* **2007**, *40*, 609.
- 4 G. M. Sheldrick, *Acta Crystallogr.*, **2008**, *A64*, 112.
- 5 The observed ESI-TOF mass spectrum is composed of three peaks assignable to the corresponding monodeuterated  $1\text{-D}_1\text{H}_3$  ( $m/z = 689$ ), dideuterated  $1\text{-D}_2\text{H}_2$  ( $m/z = 690$ ), and trideuterated  $1\text{-D}_3\text{H}_1$  ( $m/z = 691$ ) species ( $1\text{-D}_1\text{H}_3 : 1\text{-D}_2\text{H}_2 : 1\text{-D}_3\text{H}_1 = 1 : 2 : 1$ ), probably due to the H/D exchange with 2-methoxyethanol under the reaction conditions.<sup>6</sup>
- 6 T. Fukushima, T. Wada, H. Ohtsu, K. Tanaka, *Dalton Trans.* **2010**, *39*, 11526.