

Asymmetric Dimerization of Aniline-Ruthenium-Dioxolene Complex Driven by Stepwise PCET

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References

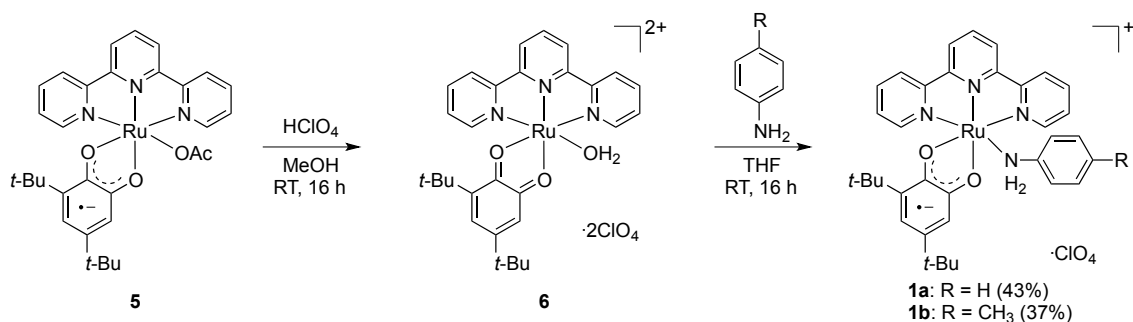
General

For single crystal X-ray crystallographic analysis, the intensity data were collected on a Rigaku Saturn 724+ CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070 \text{ \AA}$). The structures were solved by a direct method (SHELXT-2014/5)^[S1] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-2014/7).^[S1] Cyclic voltammograms were recorded on a BAS ALS model 660E electrochemical analyzer, using a glassy carbon disk electrode (7.1 mm^2) and Pt wire as the working and counter electrodes, respectively, together with an Ag/AgNO₃ reference electrode calibrated with respect to an SCE reference electrode. Electrospray ionization mass spectrometry (ESI-MS) was performed using a JEOL JMS-T100LP instrument. Electronic absorption spectra were measured on a Shimadzu UV-3600 spectrometer. Electron paramagnetic resonance (EPR) spectra were obtained on a Bruker E500 spectrometer equipped with an Oxford ESR900 cryostat at the Institute for Molecular Science. The g -value was calibrated by using an Mn(II) reference. Elemental analyses were performed on Yanaco MT-5, MT-6, and J-Science Lab JM-10 apparatuses at the Organic Elemental Analysis Research Center of the Graduate School of Pharmaceutical Sciences of Kyoto University. Infrared absorption (IR) spectra were obtained for the samples prepared as KBr pellets on a JASCO FT/IR-4100 spectrometer.

Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industry Ltd., and Merck KGaA. Alumina gel for column chromatography was washed with pure water, MeOH, and acetone, and dried *in vacuo* before use. All other chemicals were of reagent grade and used without any further purification.

Synthetic Procedure

- Syntheses and physical properties of complexes **1a,b**.



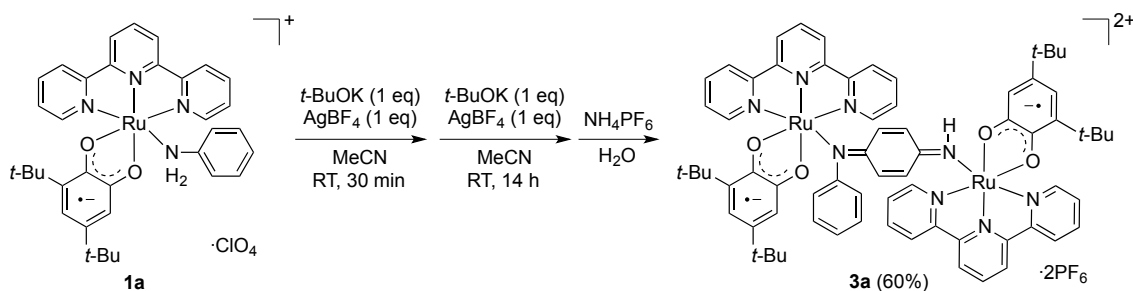
Synthesis of the aniline complex **1a·ClO₄**

To the solution of [Ru(terpy)(dbsq)(OAc)] **5** (500 mg, 815 μmol) in MeOH (15 mL), perchloric acid (5 μL) was added slowly. The resultant mixture was stirred at room temperature for 16 h, concentrated under reduced pressure to remove MeOH, and extracted with CH₂Cl₂. The CH₂Cl₂ solution was washed with water, dried on anhydrous Na₂SO₄, filtrated, and concentrated *in vacuo* to give the crude product of the aqua complex [Ru(terpy)(dbq)(OH₂)](ClO₄)₂ **6**. To the solution of the crude compound **6** in THF (50 mL), aniline (750 μL , 8.21 μmol) was added. The resultant mixture was stirred at room temperature for 16 h and concentrated *in vacuo*. After Et₂O was added to the residue, the resultant precipitate was collected by filtration and purified by column chromatography on alumina gel (acetone:MeOH = 90:10). The pure compound **1a·ClO₄** (261 mg, 349 μmol) was crystallized from mixed solution of acetone and aqueous NaClO₄ in 43% yield: IR (KBr, cm⁻¹): 3512, 3236, 3161, 2957, 2867, 1603, 1578, 1518, 1496, 1448, 1380, 1361, 1300, 1278, 1247, 1224, 1199, 1160, 1120, 1090, 1034, 989, 909, 855, 765, 724, 696, 671, 645, 626, 588, 575, 541, 525, 514. ESI-MS *m/z*: 648.20251 [M-ClO₄]⁺. Elemental Anal. Calcd for C₃₅H₃₈N₄O₆ClRu·H₂O: C, 54.93; H, 5.27; N, 7.32. Found: C, 55.08; H, 5.30; N, 7.40.

Synthesis of the aniline complex **1b**·ClO₄

A similar procedure to that of compound **1a** was employed to compound **5** (200 mg, 320 μmol) using *p*-toluidine instead of aniline to give compound **1b**·ClO₄ (92.4 mg, 121 μmol) in 37% yield: IR (KBr, cm⁻¹): 3439, 3072, 2957, 2905, 2868, 1602, 1581, 1515, 1449, 1381, 1361, 1297, 1279, 1248, 1225, 1199, 1121, 1108, 1035, 988, 858, 817, 768, 743, 726, 671, 625, 555, 540, 514. ESI-MS *m/z*: 662.21518 [M-ClO₄]⁺. Elemental Anal. Calcd for C₃₆H₄₀N₄O₆ClRu·H₂O: C, 55.49; H, 5.43; N, 7.19. Found: C, 55.33; H, 5.34; N, 7.28.

- Synthesis and physical properties of complex **3a**·2PF₆.



To the solution of compound **1a**·ClO₄ (50.0 mg, 66.9 μmol) in MeCN (15 mL), the solutions of *t*-BuOK (7.51 mg, 66.9 μmol) in MeOH (252 μL) and of AgBF₄ (13.0 mg, 66.9 μmol) in MeCN (305 μL) were added successively. After the resultant mixture was stirred at room temperature for 30 min, the solutions of *t*-BuOK (7.51 mg, 66.9 μmol) in MeOH (252 μL) and of AgBF₄ (13.0 mg, 66.9 μmol) in MeCN (305 μL) were added to the mixture slowly and successively. After being stirred at room temperature for 14 h, the mixture was filtrated through celite, and the solvent was evaporated. The residue was purified by column chromatography on alumina gel (gradient elution from acetone/MeOH = 95:5 to acetone/MeOH = 80:20). The pure compound **3a**·2PF₆ (32.0 mg, 20.2 μmol) was crystallized from mixed solution of acetone and aqueous NH₄PF₆ in 60% yield: IR (KBr, cm⁻¹): 3460, 2957, 2905, 2869, 1583, 1515, 1485, 1449, 1384, 1362, 1282, 1236, 1203, 1099, 1050, 1037, 989, 968, 846, 768, 754, 686, 673, 646, 626, 558. ESI-MS *m/z*: 646.18843 [M-2PF₆]²⁺. Elemental Anal. Calcd for C₇₀H₇₂N₈O₄F₁₂P₂Ru₂·2H₂O: C, 51.98; H, 4.74; N, 6.93. Found: C, 51.85; H, 4.74; N, 6.80.

Crystallographic data

The crystal of complex **3a** used for the single crystal X-ray analysis was obtained by slow diffusion of Et₂O vapor into a 1,2-dichloroethane solution of **3a**·2ReO₄ at 4 °C. Although various conditions were applied, only thin platelet crystals were obtained in case of the Et₂O/1,2-dichloroethane vapor diffusion process.

The selected crystal was mounted onto a loop. A measurement of the crystal was made on a Rigaku Saturn 724+ CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71070$ Å) at -110 °C. Final cell parameters were obtained from a least-squares analysis of reflections with $I > 2\sigma(I)$. Space group determination was made on the basis of systematic absences, a statistical analysis of intensity distribution, and the successful solution and refinement of the structures. An empirical absorption correction resulted in acceptable transmission factors. The data were corrected for Lorentz and polarization factors. As shown by crystal structure analysis, the crystals contained a considerable amount of crystal solvents and disordered counter anions whose fluctuation weakened the intensities of higher angle reflections reflected by the completeness smaller than 0.98 at 1.04 Å resolution.

All the calculations were carried out using shelXle and SHELXL-2014/7.^[S1] The structures were solved by direct methods and expanded using Fourier and difference Fourier techniques. Two complex cations, four perrhenate ions, and four crystal solvents (two Et₂O and two 1,2-dichloroethane) were independent. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of complex cation were located at calculated positions. In the refinement procedure, the structures of complex cations are adequately determined whereas several counter anions and crystal solvents showed considerable disorder. The still remaining electron densities are treated by using PLATON/SQUEEZE program at the final stage of the refinement. The final least square refinement affords a structure model with a reasonable atom connectivity, where the R_1 and wR_2 values of 0.0706 and 0.2098, respectively. However, because of the low crystal quality and accompanying absence of the diffraction at high angle region, the resultant crystal structure contains considerable bond length ambiguity and elongated displacement parameters.

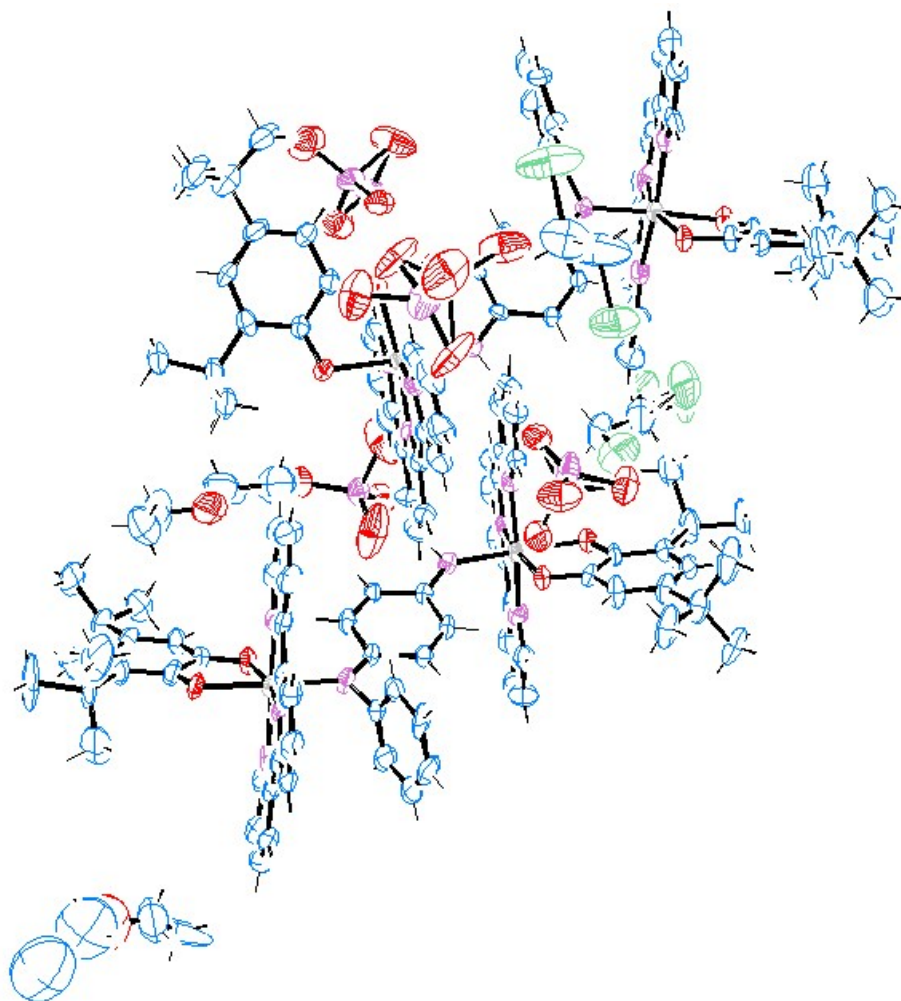


Figure S1. ORTEP drawing of the asymmetric unit in the preliminary crystal structure of complex **3a**·2ReO₄ at 30% probability level.

UV/Vis/NIR, MS, CV, and EPR spectra

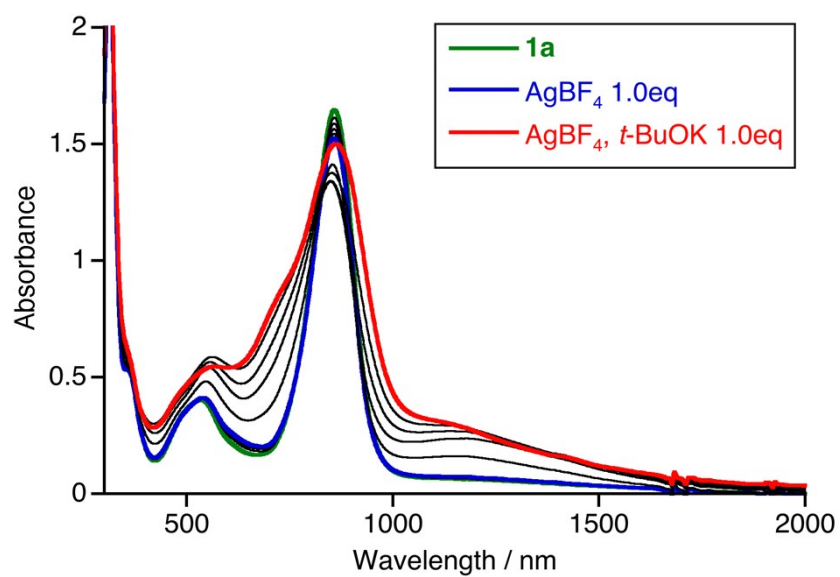


Figure S2. Electronic absorption spectra of complex **1a** before and after the successive addition of 1 equiv. of AgBF_4 and 1 equiv. of *t*-BuOK in CH_3CN .

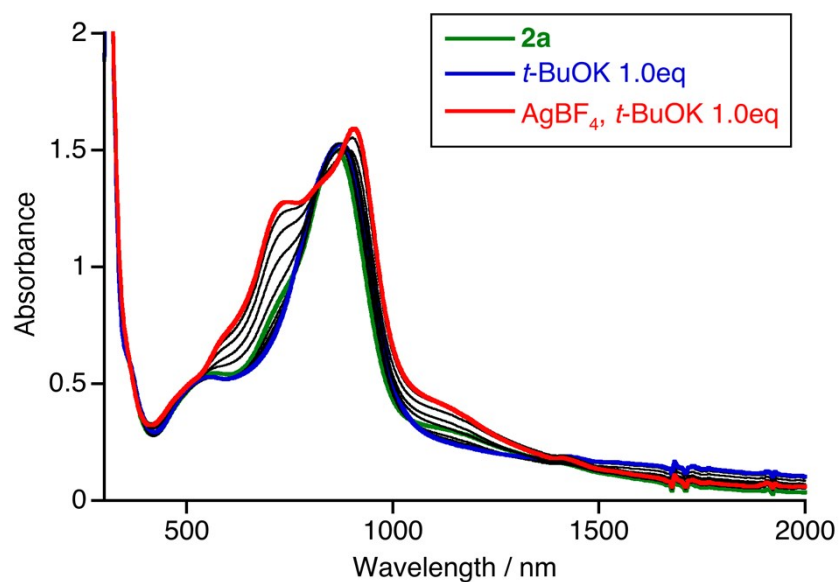


Figure S3. Electronic absorption spectra of complex **2a** before and after the successive addition of 1 equiv. of *t*-BuOK and 1 equiv. of AgBF_4 in CH_3CN .

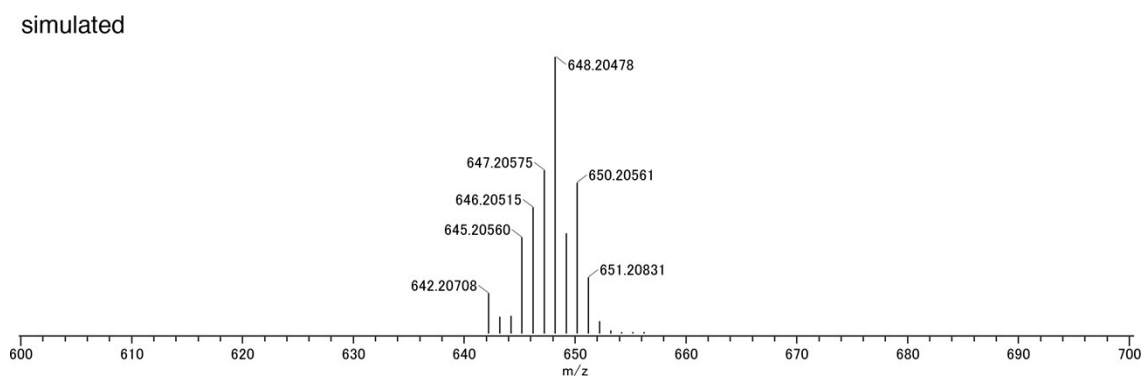
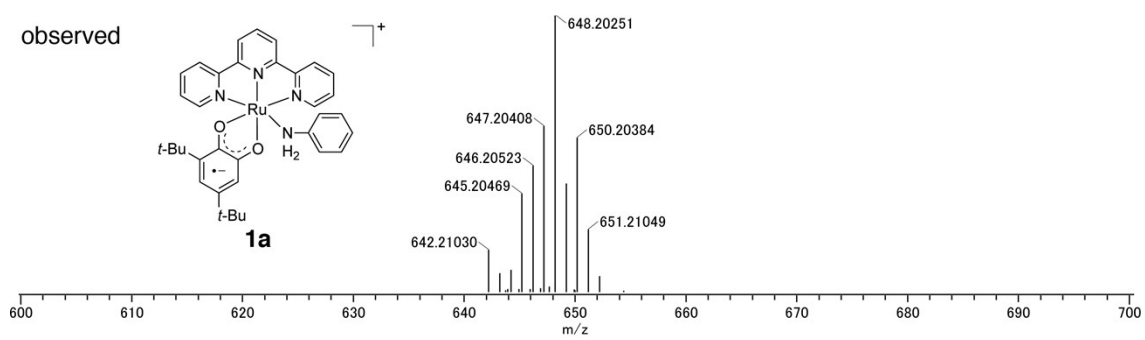


Figure S4. ESI-MS spectrum of complex **1a** in acetone.

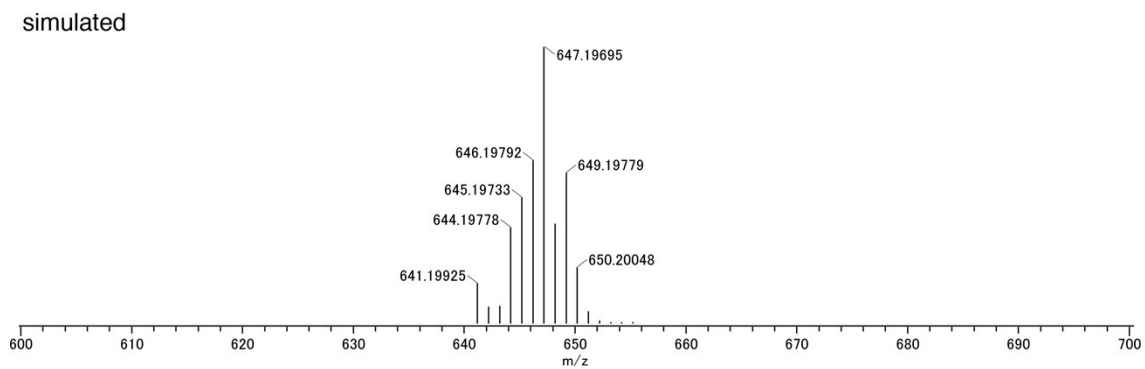
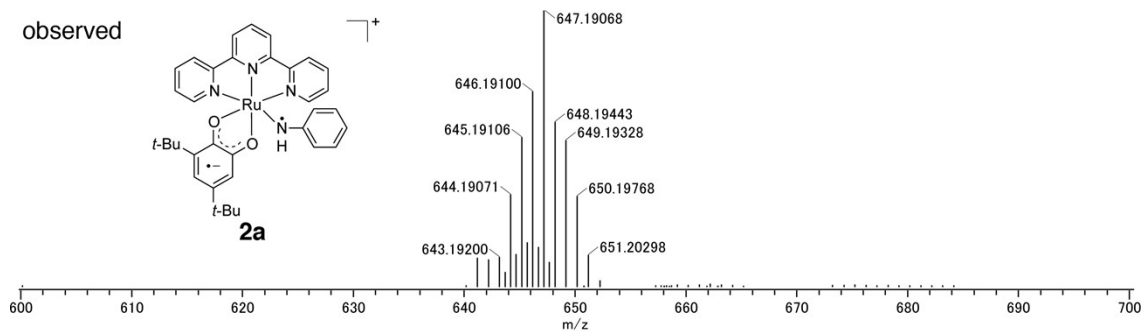


Figure S5. ESI-MS spectrum of complex **2a** in acetone.

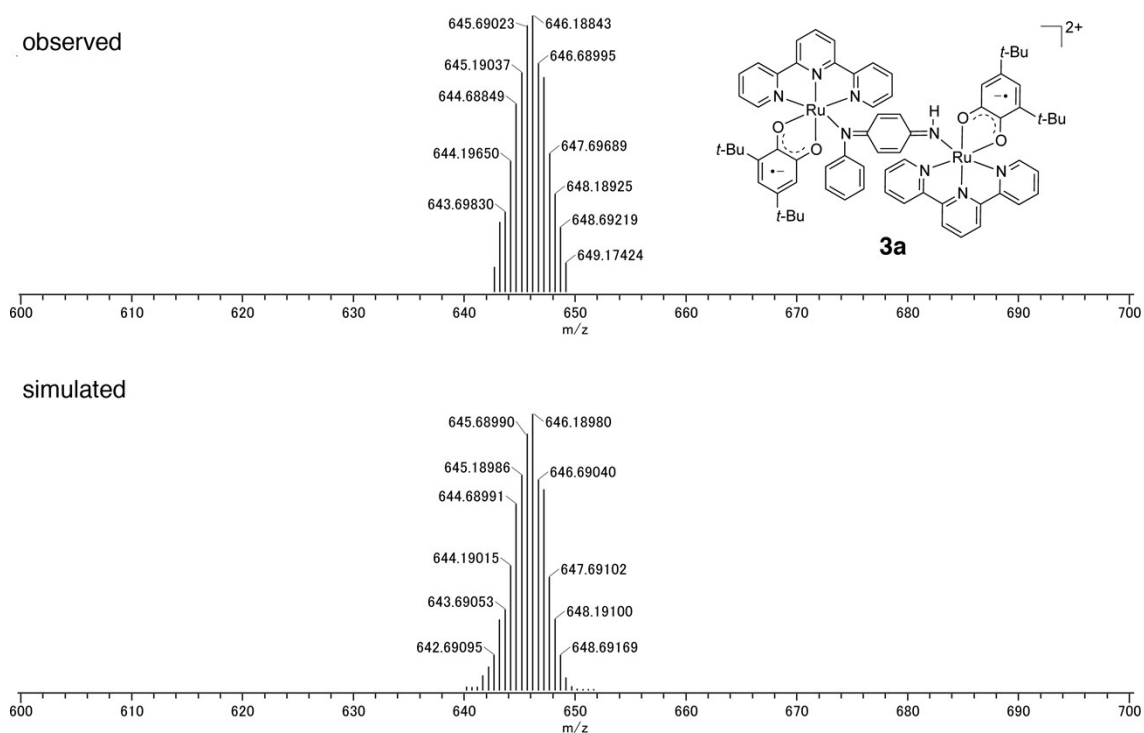


Figure S6. ESI-MS spectrum of complex **3a** in acetone.

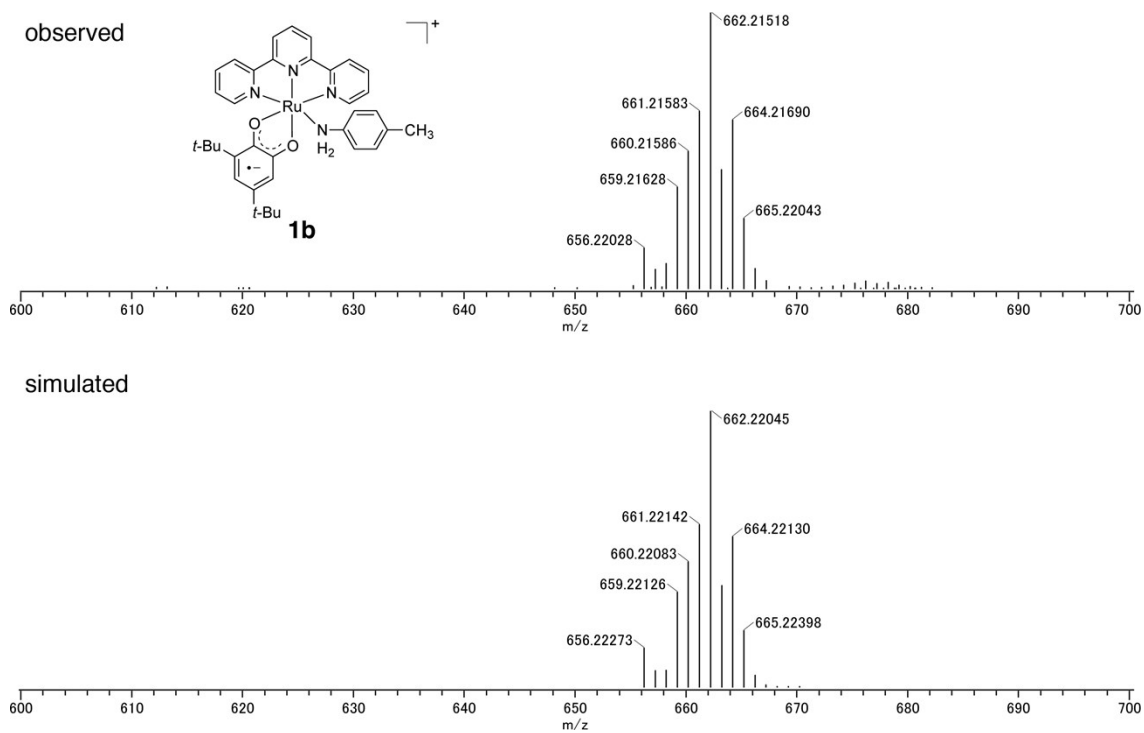


Figure S7. ESI-MS spectrum of complex **1b** in acetone.

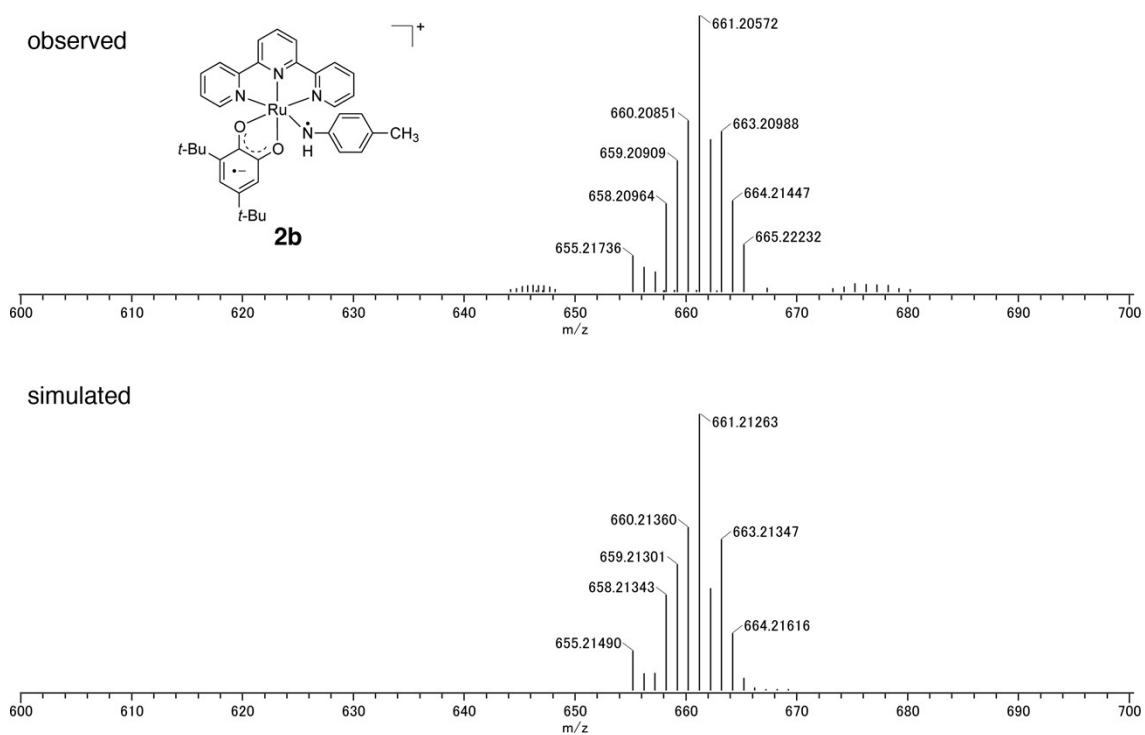


Figure S8. ESI-MS spectrum of complex **2b** in acetone.

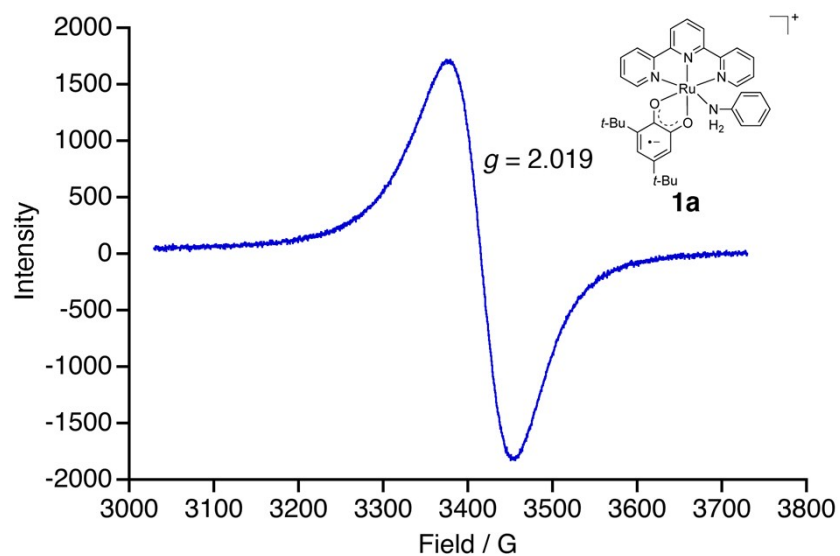


Figure S9. EPR spectrum of complex **1a** (1 mM frozen solution in MeCN, 4 K).

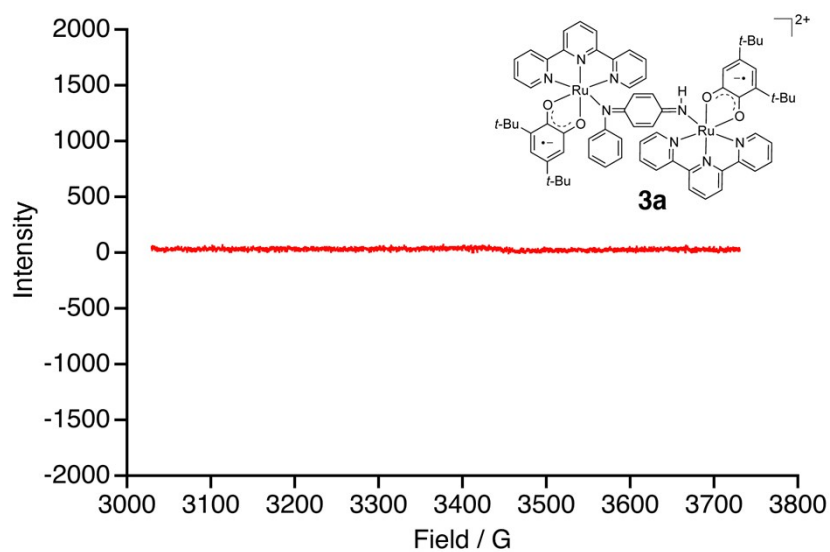


Figure S10. EPR spectrum of complex **3a** (solid powder, 4 K).

References and Notes

- [S1] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.