

**Efficient Access of Phenyl-Spaced 5,5'-Bridged Dinuclear Ruthenium Metal Complexes  
and the Effect of Dynamic Ligand Exchange on Catalysis**

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## 1. Chemicals

5-Bromo-1,10-phenanthroline<sup>[1]</sup>, [Ru(tbbpy)<sub>2</sub>Cl<sub>2</sub>]<sup>[2]</sup> and [Pt(DMSO)<sub>2</sub>Cl<sub>2</sub>]<sup>[3]</sup> were synthesized according to literature procedures. All reagents were purchased from commercial suppliers (list below) and used without further purification. All solvents were distilled before use. All <sup>1</sup>H NMR signals were assigned using 2D-NMR techniques.

	Supplier	Purity
1,4-bis(4,4,4,4-tetramethyl-1,2,3-dioxoborolan-2-yl)benzene	Sigma Aldrich	97%
K <sub>2</sub> CO <sub>3</sub>	ABCR	99%
Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	Sigma Aldrich	98%
NH <sub>4</sub> PF <sub>6</sub>	Sigma Aldrich	>95%
deuterated solvents	Sigma Aldrich	--
solvents for absorption and emission studies	Sigma Aldrich	Roth® ROTIPURE® UV/IR grade
chloroform	VWR	technical
ethylene glycol	VWR	technical, >98%
ethanol	VWR	technical
dry DMSO	Sigma Aldrich	anhydrous 99.9%
acetone	VWR	technical
methanol	VWR	technical
acetonitrile	Sigma Aldrich	HPLC grade

## 2. Preparation of catalytic mixtures

In a 21 mL schlenk tube, sealed with a standard NS14 rubber septum, 0.14 µmol of the **Rup(ph)pPtX<sub>2</sub>**-complex (X = Cl, I) was added by addition of the respective volume (varying volume due to varying concentration of the stock solution) of a dichloromethane/**Rup(ph)pPtX<sub>2</sub>** (X = Cl, I) stock solution followed by evaporation of the solvent outside of the glovebox. In case additional salts (e.g. TBAI, TBACl) were used during catalysis, they were added at this stage. After that, introducing the tube in the glovebox and adding 7.5 mL of an acetonitrile, triethylamine, water mixture (v:v:v = 6:3:1) yielded the respective 70 µM catalyst concentration. In the case of Hg addition, this was added after complete addition of the solvent. The tube was finally sealed with a NS14 rubber septum. Irradiation of the catalytic mixtures with visible light (2 LED-sticks, λ = 470 ± 20 nm, 45 ± 5 mW·cm<sup>-1</sup>, suitable to excite the <sup>1</sup>MLCT-transition of the complexes) was conducted outside of the glovebox for defined time intervals. Subsequent analysis of the headspace by gas chromatography determined the amount of hydrogen produced. By multiplying the TON with 0.14 µmol, the produced amount of hydrogen can be calculated. All data points were determined at least twice.

## 3. Reactor design

The reactor was made out of steel and the design (length = 20.5 cm; width = 20 cm; height = 20 cm) is depicted in Figure S15. The schlenk tube was fixed in the middle (distance to the walls d = 9 cm) and two LED-sticks were placed in varying positions around the tube. During irradiation, the schlenk tube was cooled by air using two air coolers per side (diameter = 9.2 cm with a power of 50.0 m<sup>3</sup> each), in total four coolers. The temperature and the pressure of the catalytic mixture during catalysis was not determined. The two LED-sticks

( $\lambda = 470 \pm 20$  nm, per LED-stick  $45 \pm 5$  mW·cm<sup>-1</sup>, emission spectra see Figure S24) were in close proximity to the schlenk tube (distance  $d = 0$  cm). We therefore assume that the photon flux of the LED-sticks is identical to the irradiation power of the sample. However, since the LED-sticks (total length of the LED-area of 11 cm) consists of single LED-points and are placed on a circuit board (length  $l = 30$  cm) that is higher than the catalytic solution (height  $h =$  ca. 5.5 cm), the LED stick was adjusted so that the solution was completely irradiated.

## 4. Synthesis

### 4.1 1,4-bis(1,10-phenanthroline-5-yl)benzene **p(ph)p**

1.0 g (4.0 mmol, 2.0 eq.) 5-Bromo-1,10-phenanthroline, 0.66 g (2.0 mmol, 1.0 eq.) 1,4-bis(4,4,4,4-tetramethyl-1,2,3-dioxoborolan-2-yl)benzene, 1.7 g (12 mmol, 6.0 eq.)  $K_2CO_3$  and 0.14 g (10 mol%)  $[Pd(PPh_3)_2Cl_2]$  were suspended in 150 mL anhydrous, degassed DMSO in a pressure vial (glovebox). After stirring at 100 °C for 48 h the solvent was removed by distillation under vacuum at 115 °C. The brown residue was dissolved/suspended in 300 mL of chloroform and placed for 30 min in an ultrasonic bath. After filtration over a plug of celite, the solvent was removed. The beige residue was washed with small amounts of hot ethanol to remove  $PPh_3$  and  $PPh_3O$ . Recrystallization in chloroform yields the pure product in 71% (617 mg, 1.42 mmol), comparable to that reported in literature (75%).<sup>[1]</sup>

**$^1H$  NMR (400 MHz,  $CDCl_3$ ):**  $\delta$  = 9.27 (td,  $J$  = 4.6, 1.8 Hz, 4  $H_{2,9}$ ), 8.46 (dd,  $J$  = 8.4, 1.8 Hz, 2  $H_{4,7}$ ), 8.34 (dd,  $J$  = 8.1, 1.8 Hz, 2  $H_{4,7}$ ), 7.89 (s, 2  $H_6$ ), 7.75 (s, 4  $H_{ph}$ ), 7.70 (ddd,  $J$  = 16.3, 8.2, 4.3 Hz, 4  $H_{3,8}$ ).

**$^{13}C$  NMR (101 MHz,  $CDCl_3$ ):**  $\delta$  = 150.60, 150.38, 146.52, 145.87, 138.85, 138.45, 136.29, 134.68, 130.43, 128.28, 127.97, 126.95, 123.69, 123.14.

**ESI-HRMS:** 435.16024  $[M + H]^+$  (calculated: 435.16042 m/z).

### 4.2 $[(tbbpy)_2Ruphen(ph)phen](PF_6)_2$ **Rup(ph)p**

0.20 g (0.46 mmol, 1.0 eq.) **p(ph)p** were suspended in 50 mL each of deaerated ethylene glycol and ethanol and heated at 130 °C under argon until the ligand completely dissolved (30 minutes). A solution of 0.30 g (0.46 mmol, 1.0 eq.)  $[(tbbpy)_2RuCl_2]$  in 50 mL of deaerated ethanol was added dropwise within 90 minutes. The red solution was refluxed for further 2 h to complete the reaction. Removal of ethanol, addition of water and addition of 20 eq.  $NH_4PF_6$ , dissolved in 3 mL of water, yields a fine red solid which was filtrated through a Por4 glass frit. The solid was washed with an excess of water and diethyl ether. The crude product was dissolved in acetone and filtered through a Por4 glass frit to remove unreacted ligand. Removal of the solvent yields the crude mixture of the mononuclear  $[(tbbpy)_2Ru(p(ph)p)](PF_6)_2$  **Rup(ph)p** complex as the main product and the dinuclear  $[(tbbpy)_2Ru(p(ph)p)Ru(tbbpy)_2](PF_6)_4$  **Rup(ph)pRu** as side product. Further purification could be achieved using size exclusion chromatography (SEPHADEX® as stationary phase) using CAM (CAM = chloroform:acetone:methanol / 160:190:150 mL) as mobile phase. The pure product  $[(tbbpy)_2Ru(p(ph)p)](PF_6)_2$  was obtained in a yield of 63.8% (400 mg, 29 mmol).

**$^1H$  NMR (400 MHz,  $CD_3CN$ ):**  $\delta$  = 9.18 (m, 2  $H_{2',9'}$ ), 8.64 (dd,  $J$  = 8.4, 1.2 Hz, 2  $H_{2,9}$ ), 8.53 (d,  $J$  = 2.4 Hz, 2  $H_{3bpy}$ ), 8.51 – 8.44 (m, 4  $H_{3bpy,4',7'}$ ), 8.32 (s, 1  $H_6$ ), 8.10 (m, 2  $H_{4,7}$ ), 8.00 (s, 1  $H_{6'}$ ), 7.89 – 7.69 (m, 10  $H_{ph,3,3',8,8',6bpy}$ ), 7.53 – 7.44 (m, 4  $H_{6'bpy,5bpy}$ ), 7.25 (m, 2  $H_{5'bpy}$ ), 1.45 (d,  $J$  = 2.1 Hz, 18  $H_{tb}$ ), 1.38 (d,  $J$  = 0.7 Hz, 18  $H_{tb}$ ).

**$^{13}C$  NMR (101 MHz,  $CD_3CN$ ):**  $\delta$  = 163.56, 163.43, 158.06, 158.01, 157.79, 153.11, 153.06, 152.18, 152.11, 152.04, 152.00, 150.59, 150.49, 149.26, 148.29, 145.98, 145.22, 141.16, 140.09, 139.20, 138.30, 137.80, 137.31, 136.11, 136.01, 131.55, 131.35, 131.28, 131.22, 129.42, 128.92, 128.84, 127.98, 127.32, 126.84, 125.54, 125.42, 125.36, 125.01, 124.50, 122.47, 122.44, 122.39, 36.30, 36.21, 30.46, 30.38.

**MALDI-HRMS:** 1217.40743  $[M - PF_6]^+$  (calculated: 1217.40902 m/z), 2579.78624  $[2 M - PF_6]^+$  (calculated: 2579.78737 m/z).



#### 4.3 [(tbbpy)<sub>2</sub>Ruphen(ph)phenRu(tbbpy)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> **Rup(ph)pRu**

50 mg (0.11 mmol, 1.0 eq.) phen(ph)phen was suspended in 30 mL each of deaerated ethylene glycol and ethanol and heated at 130 °C for 5 minutes under argon atmosphere. A solution of 160 mg (0.23 mmol, 2.1 eq.) [(tbbpy)<sub>2</sub>RuCl<sub>2</sub>] was added dropwise within a period of 90 minutes. The red/brown solution was then refluxed for another 4 h to complete the reaction. Removing the ethanol in vacuo and adding of 100 mL of water along with dropwise addition of 20 eq. NH<sub>4</sub>PF<sub>6</sub>, dissolved in 3 mL of water yielded a red solid which was then filtrated through a Por4 glass frit. The solid was washed with 100 mL of water and 100 mL of diethyl ether. The crude product was dissolved in acetone and filtered once again through a Por4 glass frit to remove unreacted ligand. Removal of the solvent and purification using size exclusion chromatography (SEPHADEX<sup>®</sup> serving as stationary phase) with CAM (CAM = chloroform:acetone:methanol / 160:190:150 mL) as eluent yielded the pure product in 91% (223 mg, 0.10 mmol) yield.

**<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):** δ = 8.63 (m, 4 H<sub>2,2',9,9'</sub>), 8.54 (d, J = 2.2 Hz, 4 H<sub>3bpy</sub>), 8.50 (d, J = 2.2 Hz, 4 H<sub>3'bpy</sub>), 8.31 (s, 2 H<sub>6</sub>), 8.11 (m, 4 H<sub>4,7</sub>), 7.88 (s, 4 H<sub>ph</sub>), 7.83 – 7.69 (m, 8 H<sub>3,8,6bpy</sub>), 7.52 – 7.44 (m, 8 H<sub>5bpy,6'bpy</sub>), 7.28 – 7.22 (m, 4 H<sub>5'bpy</sub>), 1.45 (d, J = 3.0 Hz, 36 H<sub>tb</sub>), 1.37 (s, 36 H<sub>tb'</sub>).

**<sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN):** δ = 163.58, 163.45, 158.06, 158.01, 157.81, 153.20, 153.13, 152.18, 152.10, 152.05, 152.01, 149.27, 148.34, 140.95, 138.51, 137.35, 135.94, 131.57, 131.34, 131.19, 128.94, 127.36, 126.91, 125.56, 125.43, 125.37, 122.50, 122.47, 122.41, 36.31, 36.22, 30.46, 30.39.

**MALDI-HRMS:** 2145.63373 [M – PF<sub>6</sub>]<sup>+</sup> (calculated: 2145.63422 m/z), 4435.24373 [2 M – PF<sub>6</sub>]<sup>+</sup> (calculated: 4435.22401 m/z).

#### 4.4 [(tbbpy)<sub>2</sub>Ruphen(ph)phenPtCl<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> **Ru(ph)pPtCl<sub>2</sub>**

60 mg (0.04 mmol, 1.0 eq.) **Rup(ph)p** and 20 mg (0.047 mmol, 1.17 eq.) [PtCl<sub>2</sub>(DMSO)<sub>2</sub>] were dissolved in 35 mL degassed ethanol. The red solution was refluxed for 5 h under argon, cooled to room temperature and 50 mg (0.31 mmol, 7.7 eq.) NH<sub>4</sub>PF<sub>6</sub> dissolved in 20 mL of water were added dropwise. The red suspension was stirred for another 1 h to complete precipitation. Filtration of the suspension through a Por4 glass frit yielded the crude product which was then washed with small amounts of cold ethanol, water and diethyl ether. The crude product was purified using size exclusion chromatography (SEPHADEX<sup>®</sup> serving as stationary phase) with CAM (CAM = chloroform:acetone:methanol / 160:190:150 mL) as eluent, giving 57.3 mg (88%, 0.035 mmol) of a red powder.

**<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):** δ = 9.78 (dd, J = 5.5, 1.3 Hz, 1 H<sub>2'/9'</sub>), 9.68 (dd, J = 5.5, 1.3 Hz, 1 H<sub>2/9</sub>), 8.85 (m, 2 H<sub>4',7'</sub>), 8.64 (m, 2 H<sub>2,9</sub>), 8.54 (d, J = 2.0 Hz, 2 H<sub>3bpy</sub>), 8.51 – 8.48 (m, 2 H<sub>3'bpy</sub>), 8.33 (s, 1 H<sub>6</sub>), 8.24 (s, 1 H<sub>6'</sub>), 8.11 (m, 2 H<sub>4,7</sub>), 8.01 (m, 2 H<sub>4',7'</sub>), 7.89 (q, J = 8.3 Hz, 4 H<sub>ph</sub>), 7.83 – 7.71 (m, 4 H<sub>3,3',8,8',6bpy</sub>), 7.52 – 7.46 (m, 4 H<sub>5bpy,6'bpy</sub>), 7.26 (m, 2 H<sub>5'bpy</sub>), 1.46 (d, J = 2.3 Hz, 18 H<sub>tb</sub>), 1.38 (s, 18 H<sub>tb'</sub>).

**<sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN):** δ = 163.58, 163.45, 158.08, 158.02, 157.81, 153.18, 153.12, 152.21, 152.13, 152.06, 152.02, 149.82, 149.54, 149.29, 148.57, 148.36, 140.99, 140.69, 140.15, 138.73, 138.49, 138.08, 137.37, 136.00, 131.88, 131.44, 131.36, 131.34, 131.31, 131.20, 128.97, 128.69, 127.35, 126.95, 126.92, 126.91, 126.77, 125.56, 125.45, 125.40, 122.49, 122.46, 122.41, 36.31, 36.22, 30.46, 30.39.

**<sup>195</sup>Pt NMR (128.71 MHz, CD<sub>3</sub>CN):** δ = –2331.90.

**ESI-HRMS:** 669.19079 [M – 2 PF<sub>6</sub>]<sup>+</sup> (calculated: 669.17730 m/z).

#### 4.5 $[(\text{tbbpy})_2\text{Ruphen}(\text{ph})\text{phenPtI}_2](\text{PF}_6)_2$ **Rup(ph)pPtI<sub>2</sub>**

73.9 mg (0.054 mmol, 1.00 eq.) **Rup(ph)p** and 33.8 mg (0.056 mmol, 1.03 eq.)  $[\text{Pt}(\text{DMSO})_2\text{I}_2]$  were dissolved in 40 mL degassed ethanol. The red solution was refluxed for 5 h under argon atmosphere, cooled to room temperature and 59.5 mg (0.365 mmol, 6.76 eq.)  $\text{NH}_4\text{PF}_6$  dissolved in 20 mL of water were added dropwise. The suspension was stirred for another 1 h at room temperature to complete precipitation followed by filtration through a Por4 glass frit. The red solid was washed with cold ethanol, water and diethyl ether. The crude product was purified using size exclusion chromatography (SEPHADEX<sup>®</sup> serving as stationary phase) with CAM (CAM = chloroform:acetone:methanol / 160:190:150 mL) as eluent, giving 79.7 mg (82%, 0.044 mmol) of a red powder.

**$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta$  = 10.37 (d,  $J$  = 5.5 Hz, 1  $\text{H}_{2'/9'}$ ), 10.25 (d,  $J$  = 5.5 Hz, 1  $\text{H}_{2'/9'}$ ), 8.88 (dd,  $J$  = 16.2, 8.2 Hz, 2  $\text{H}_{4'/7'}$ ), 8.71 – 8.59 (m, 2  $\text{H}_{2/9}$ ), 8.56 – 8.47 (m, 4  $\text{H}_{3\text{bpy}/3'\text{bpy}}$ ), 8.33 (s, 1  $\text{H}_6$ ), 8.22 (s, 1  $\text{H}_6$ ), 8.16 – 8.09 (m, 2  $\text{H}_{4/7}$ ), 7.99 (t,  $J$  = 5.9 Hz, 2  $\text{H}_{3'/8'}$ ), 7.89 (s, 4  $\text{H}_{\text{ph}}$ ), 7.80 (td,  $J$  = 8.2, 5.2 Hz, 2  $\text{H}_{3/8}$ ), 7.73 (t,  $J$  = 6.0 Hz, 2  $\text{H}_{6\text{bpy}}$ ), 7.54 – 7.45 (m, 5  $\text{H}_{5\text{bpy}/6'\text{bpy}}$ ), 7.32 – 7.24 (m, 2  $\text{H}_{5'\text{bpy}}$ ), 1.46 (d,  $J$  = 2.2 Hz, 18  $\text{H}_{\text{tb}}$ ), 1.38 (s, 18  $\text{H}_{\text{tb}}$ ).

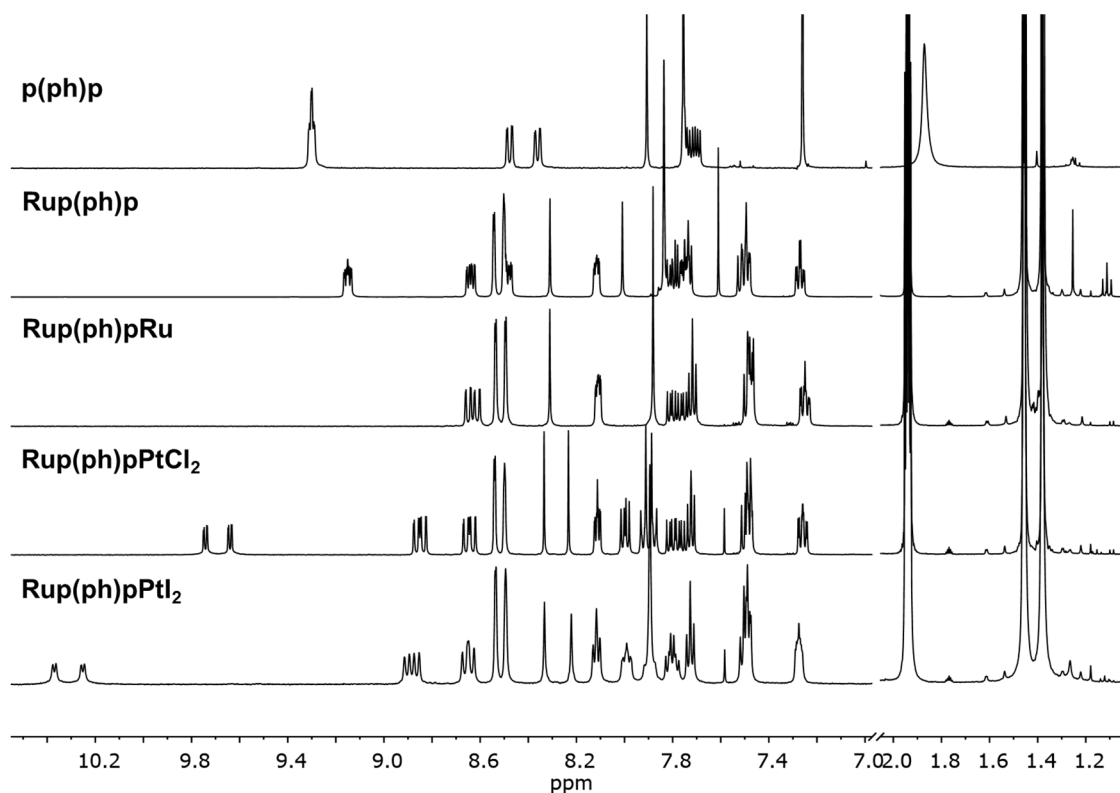
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta$  = 163.58, 163.43, 158.07, 158.02, 157.80, 153.18, 153.12, 152.67, 152.41, 152.22, 152.15, 152.06, 152.02, 149.41, 149.29, 148.41, 148.36, 140.96, 140.51, 140.21, 138.61, 138.46, 138.06, 137.38, 136.00, 131.86, 131.80, 131.46, 131.37, 131.19, 128.98, 128.89, 127.57, 127.36, 126.94, 125.56, 125.48, 125.42, 122.50, 122.46, 122.41, 36.31, 36.23, 30.47, 30.40.

**$^{195}\text{Pt}$  NMR (128.71 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta$  = –2285.46.

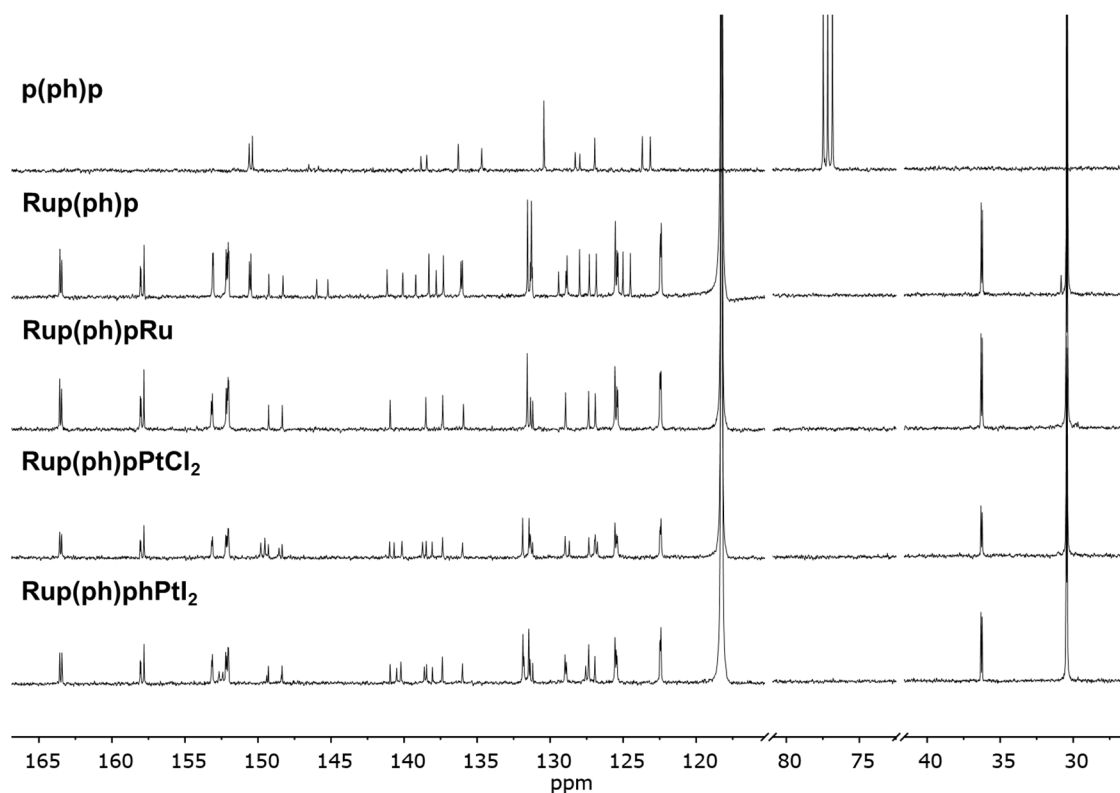
**ESI-HRMS:** 760.60374  $[\text{M} - 2 \text{PF}_6]^{2+}$  (calculated: 760.60900 m/z).

## 5. Supplementary Figures

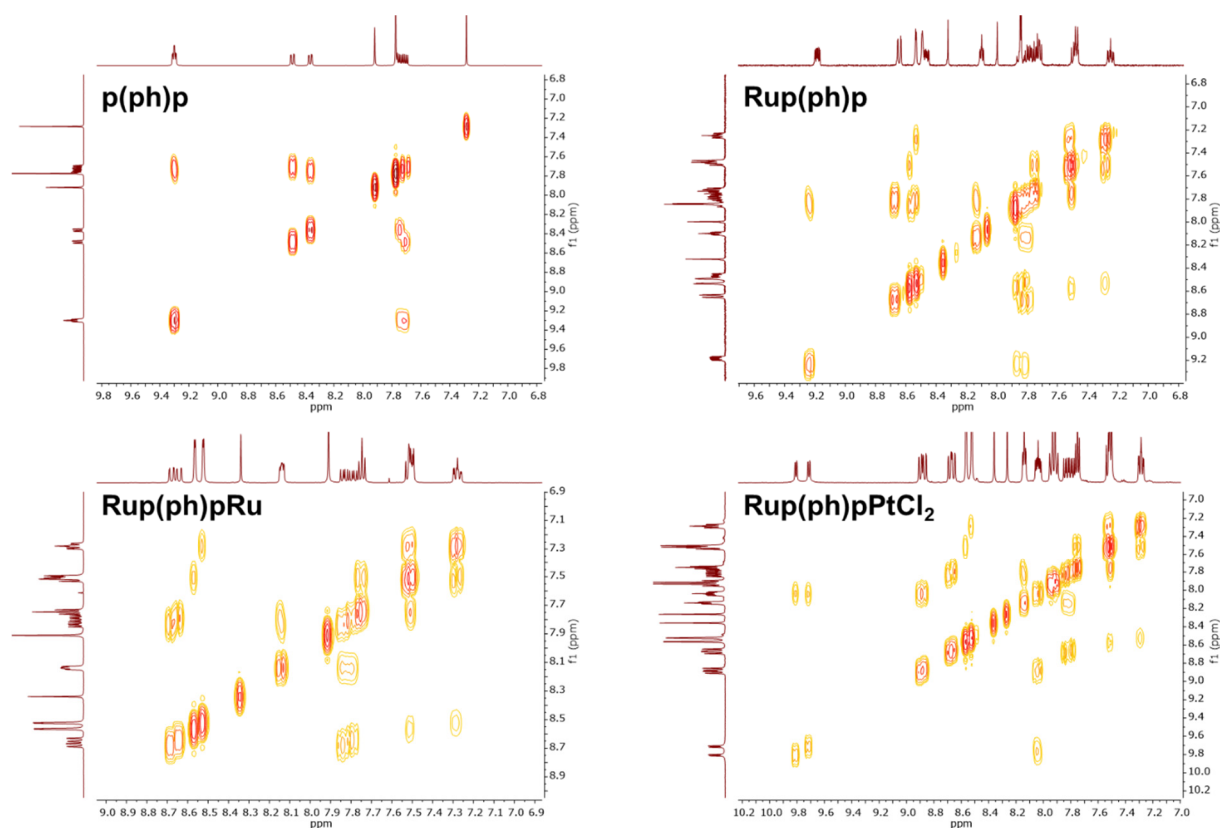
### 5.1 Structural characterization



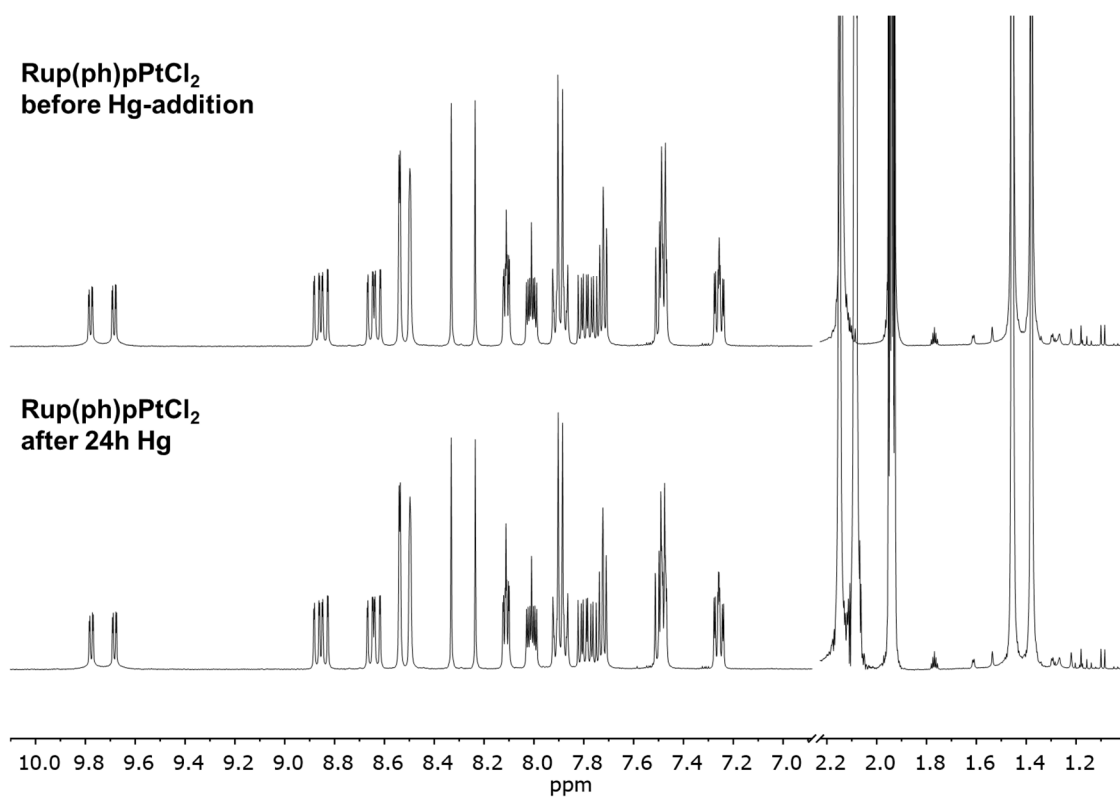
**Figure S1.**  $^1\text{H}$  NMR spectra of the ligand **p(ph)p** in  $\text{CDCl}_3$  and the complexes **Rup(ph)p**, **Rup(ph)pRu**, **Rup(ph)pPtCl<sub>2</sub>** and **Rup(ph)pPtI<sub>2</sub>** in  $\text{CD}_3\text{CN}$  at 400 MHz basis frequency at room temperature.



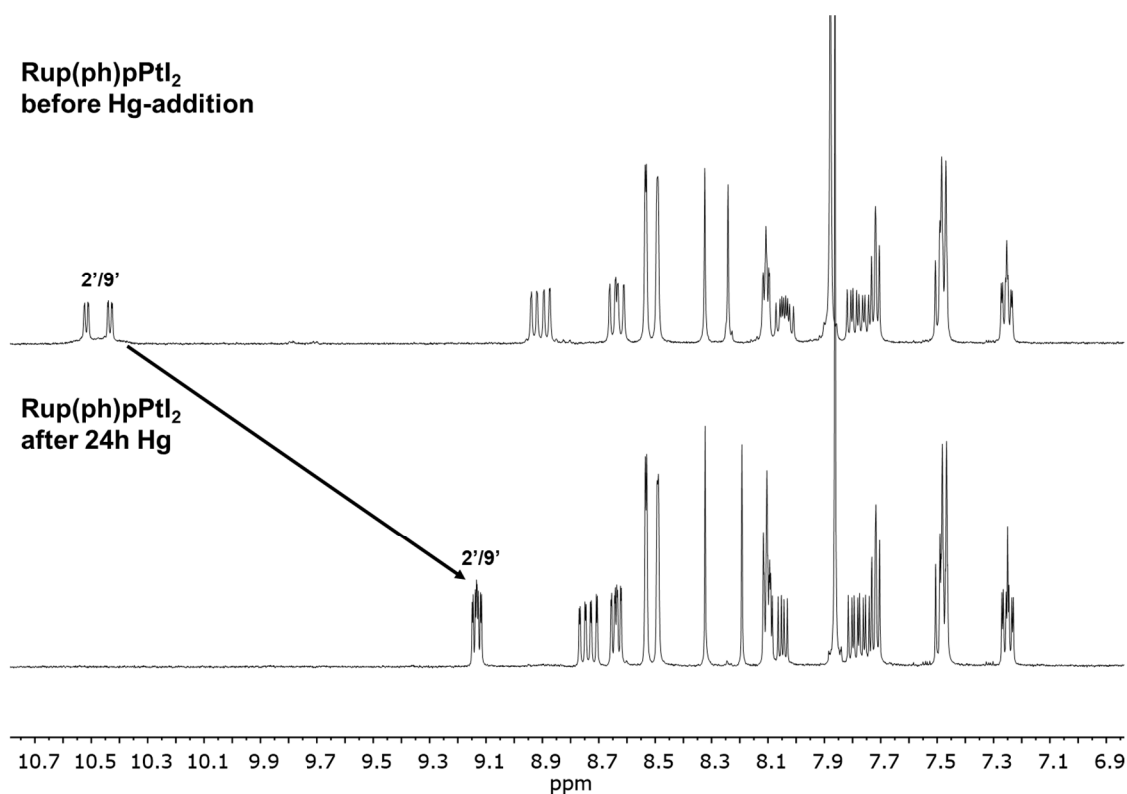
**Figure S2.**  $^{13}\text{C}$  NMR spectra of the ligand **p(ph)p** in  $\text{CDCl}_3$  and the complexes **Rup(ph)p**, **Rup(ph)pRu**, **Rup(ph)pPtCl<sub>2</sub>** and **Rup(ph)pPtI<sub>2</sub>** in  $\text{CD}_3\text{CN}$  at 101 MHz basis frequency at room temperature.



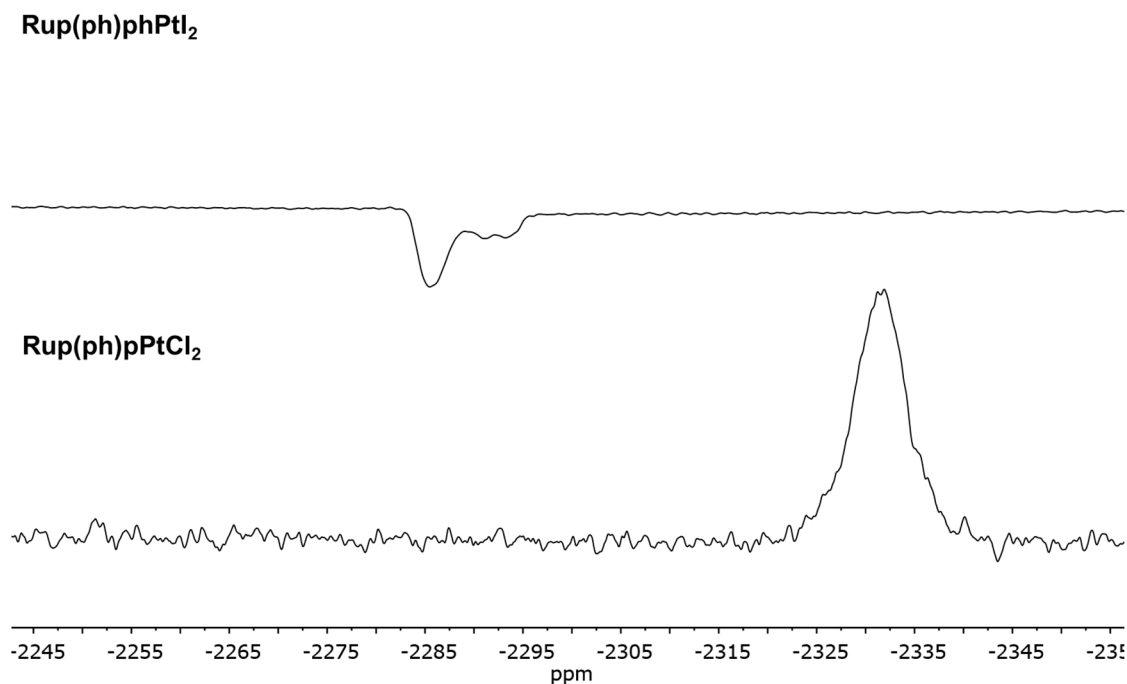
**Figure S3.** 2D-NMR spectra ( $^1\text{H}$ , $^1\text{H}$ -COSY) of the ligand **p(ph)p** in  $\text{CDCl}_3$  and the complexes **Rup(ph)p**, **Rup(ph)pRu** and **Rup(ph)pPtCl<sub>2</sub>** in  $\text{CD}_3\text{CN}$  at 400 MHz basis frequency at room temperature.



**Figure S4.**  $^1\text{H}$  NMR spectra of **Rup(ph)pPtCl<sub>2</sub>** in  $\text{CD}_3\text{CN}$  before (top) and after 24 h of stirring with five droplets of elemental mercury without irradiation (bottom) at 400 MHz basis frequency at room temperature. No instability against mercury was observed.

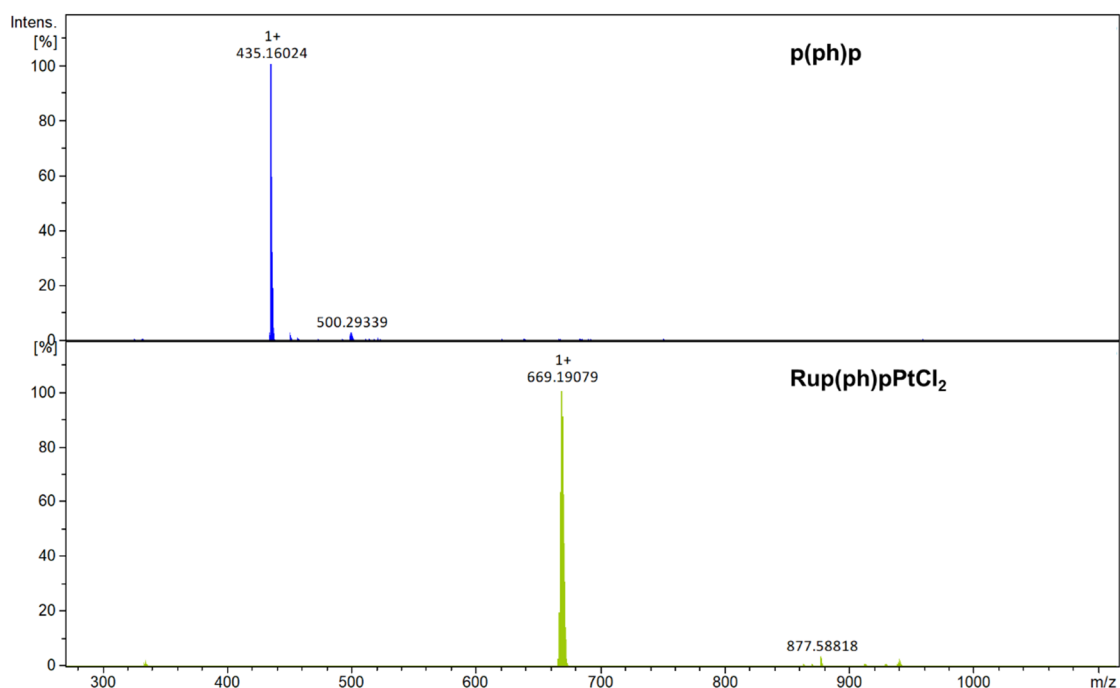


**Figure S5.**  $^1\text{H}$  NMR spectra of  $\text{Rup}(\text{ph})\text{pPtI}_2$  in  $\text{CD}_3\text{CN}$  before (top) and after 24 h of stirring with five droplets of elemental mercury without irradiation (bottom) at 400 MHz basis frequency at room temperature. Loss of the catalytic active Pt-centre can be observed by the shift of the  $2'/9'$ -proton. ESI-MS characterization supported the loss of the Pt-centre (see Figure S10).

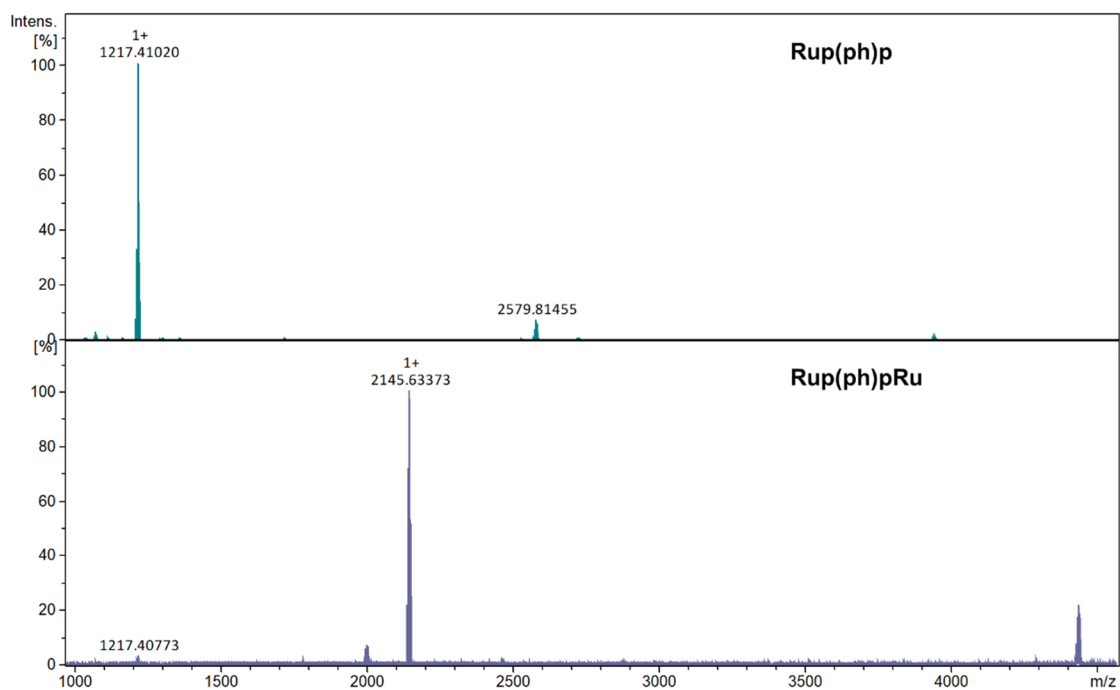


**Figure S6.**  $^{195}\text{Pt}$  NMR spectra of  $\text{Rup}(\text{ph})\text{pPtI}_2$  (top) and  $\text{Rup}(\text{ph})\text{pPtCl}_2$  (bottom) in  $\text{CD}_3\text{CN}$  at 128.71 MHz basis frequency at room temperature.

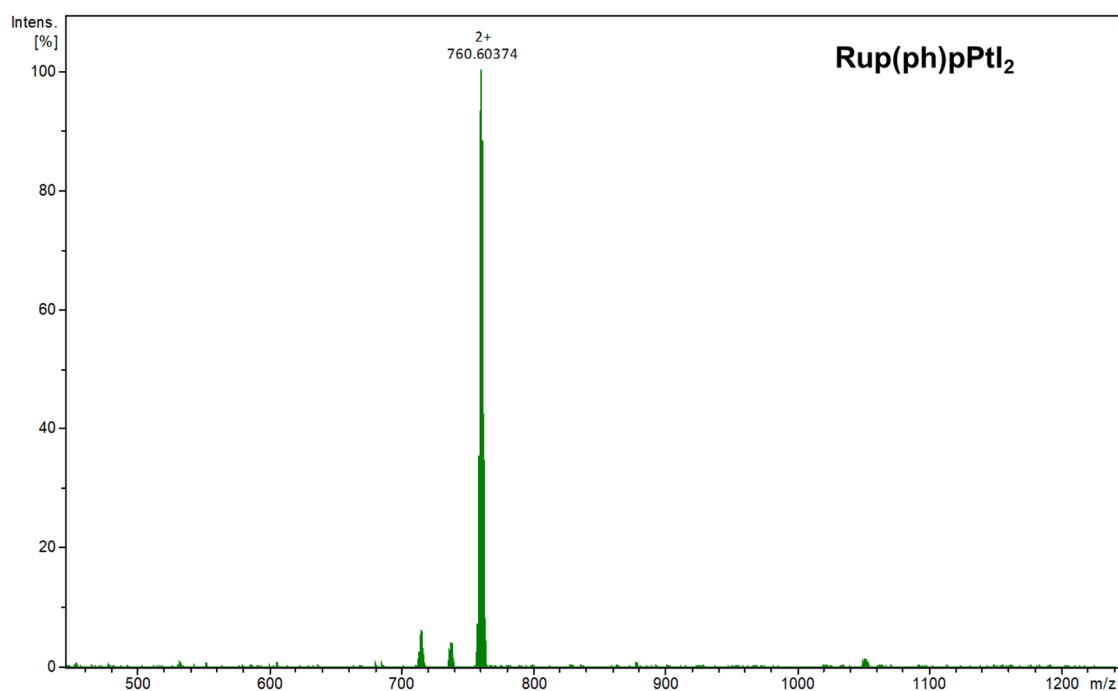
## 5.2 High resolution mass spectrometric analysis



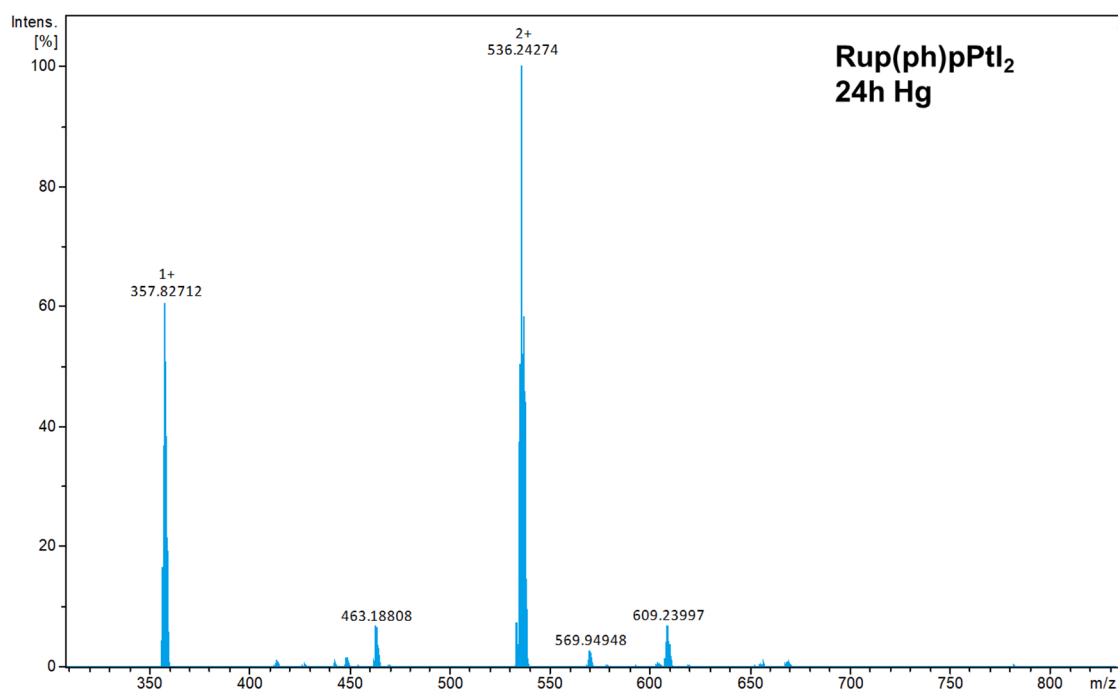
**Figure S7.** High-resolution ESI-MS spectra of **p(ph)p** ( $[M + H]^+$  calculated: 435.16042  $m/z$ ) and **Rup(ph)pPtCl<sub>2</sub>** ( $[M - 2 PF_6]^+$  calculated: 669.17730  $m/z$ ).



**Figure S8.** High-resolution MALDI-MS spectra of **Rup(ph)p** ( $[M - PF_6]^+$  calculated: 1217.40902  $m/z$ ;  $[2 M - PF_6]^+$  calculated: 2579.78737  $m/z$ ) and **Rup(ph)pRu** ( $[M - PF_6]^+$  calculated: 2145.63422  $m/z$ ;  $[2 M - PF_6]^+$  calculated: 4435.22401  $m/z$ ).

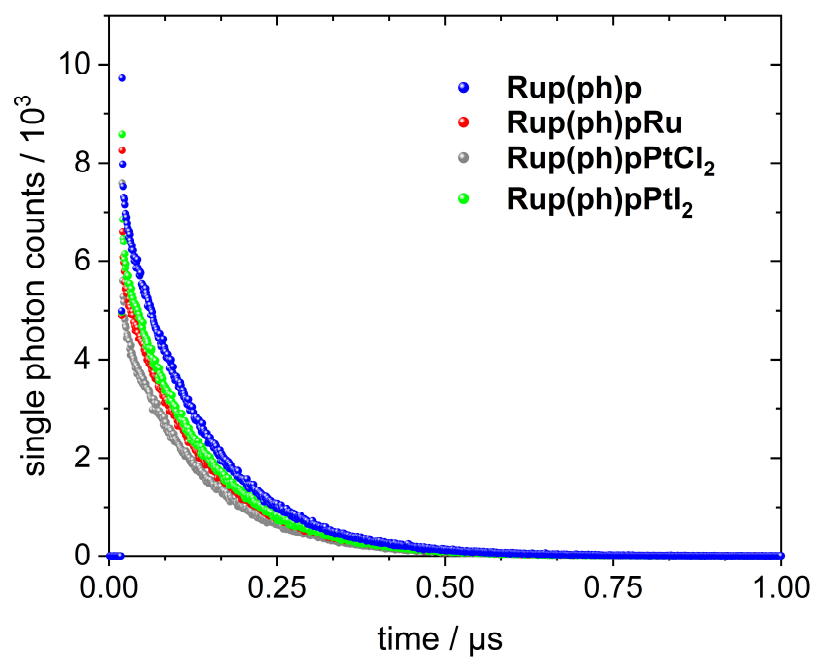


**Figure S9.** High-resolution ESI-MS spectra of **Rup(ph)pPtI<sub>2</sub>** ( $[M - 2 \text{PF}_6]^{2+}$  calculated: 760.60900 m/z).

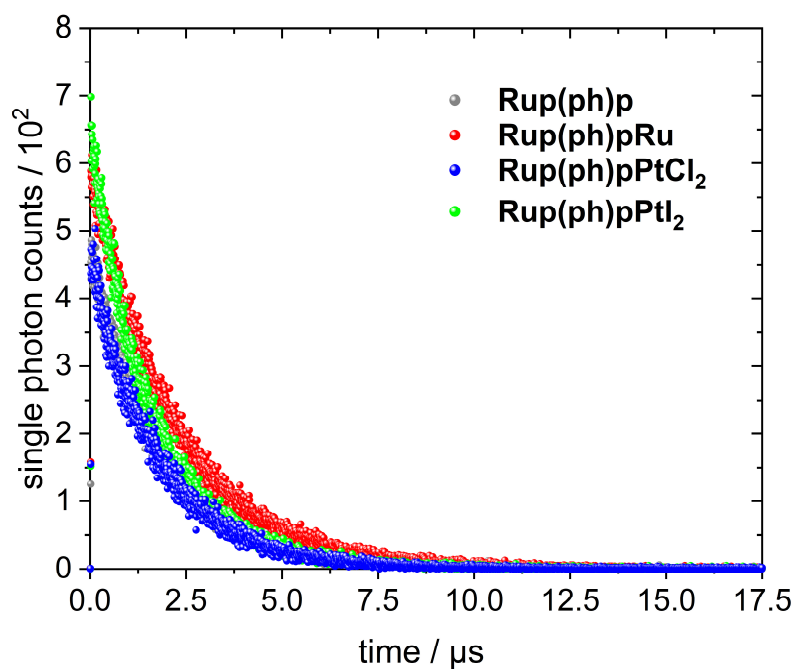


**Figure S10.** High-resolution ESI-MS spectra of **Rup(ph)pPtI<sub>2</sub>** after 24 h of stirring with five drops of mercury in deuterated acetonitrile. As Figure S5 clearly shows, the loss of the Pt-centre, the signal at 357.82712 m/z can be assigned to  $[M - e - \text{PtI}_2 - 2 \text{PF}_6]^{3+}$  (calculated: 357.81570 m/z); 536.24274 m/z can be assigned to  $[M - \text{PtI}_2 - 2 \text{PF}_6]^{2+}$  (calculated: 536.22215 m/z).

### 5.3 Photophysical characterization

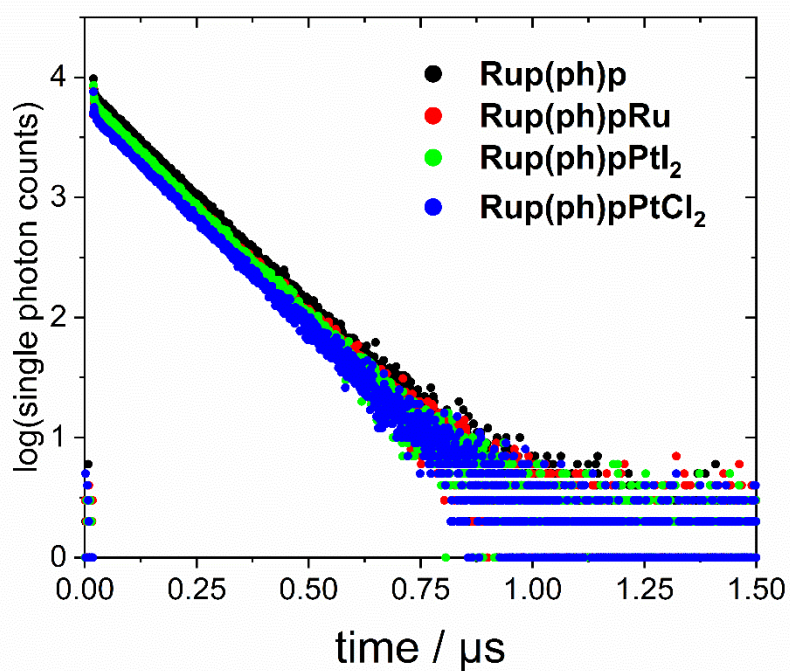


**Figure S11.** Emission lifetimes of all Ru-complexes in air-saturated acetonitrile at room temperature ( $\lambda_{\text{exc}} = 451 \text{ nm}$ ).

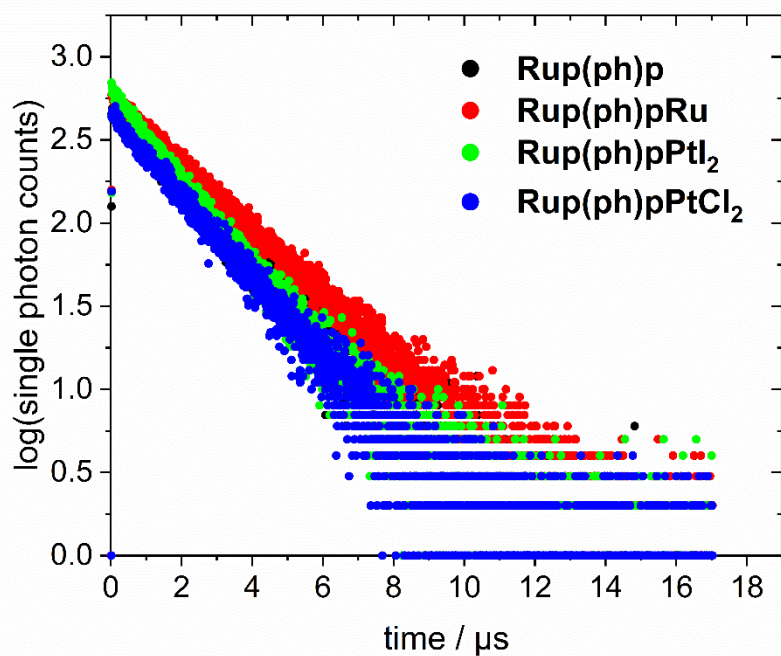


**Figure S12.** Emission lifetimes of all investigated Ru-complexes in argon-saturated, dry acetonitrile at room temperature ( $\lambda_{\text{exc}} = 451 \text{ nm}$ ).



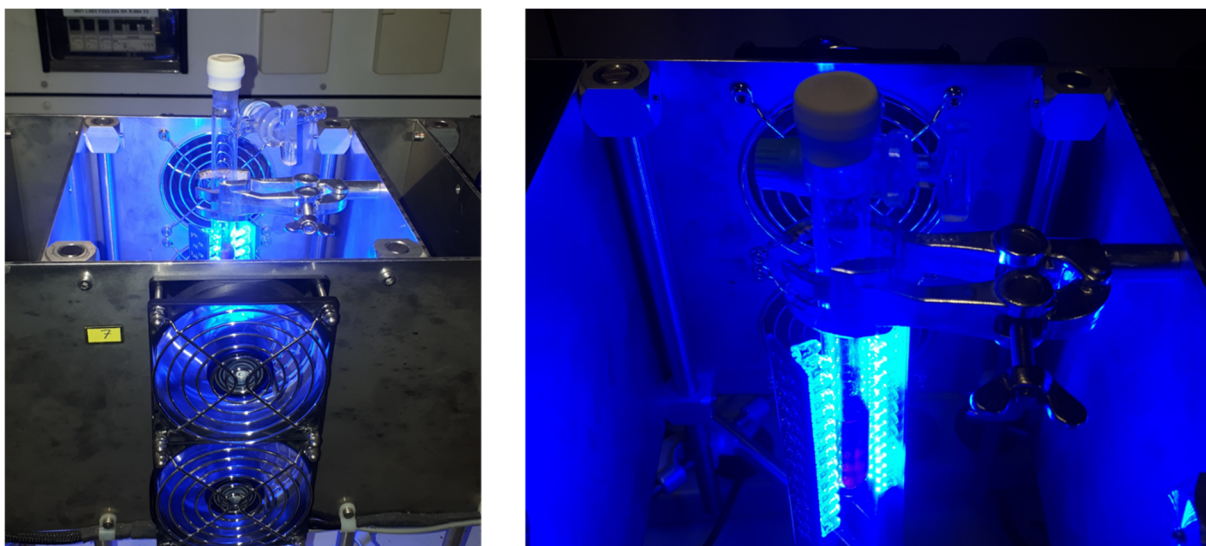


**Figure S13.** Logarithmic depiction of emission lifetimes of all Ru-complexes in air-saturated acetonitrile at room temperature. A linear decay clearly indicates a mono exponential decay ( $\lambda_{\text{exc}} = 451 \text{ nm}$ ).

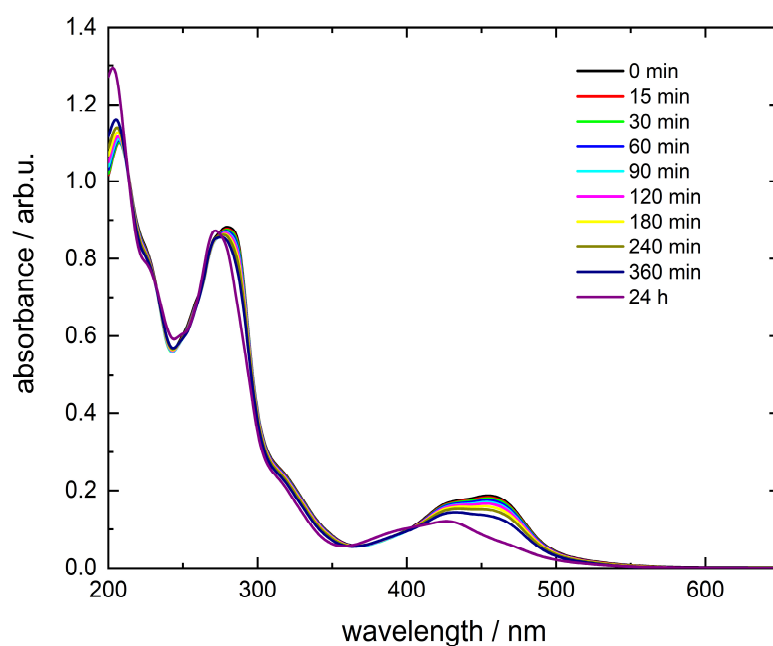


**Figure S14.** Logarithmic depiction of emission lifetimes of all Ru-complexes in argon-saturated acetonitrile at room temperature. A linear decay clearly indicates a mono exponential decay ( $\lambda_{\text{exc}} = 451 \text{ nm}$ ).

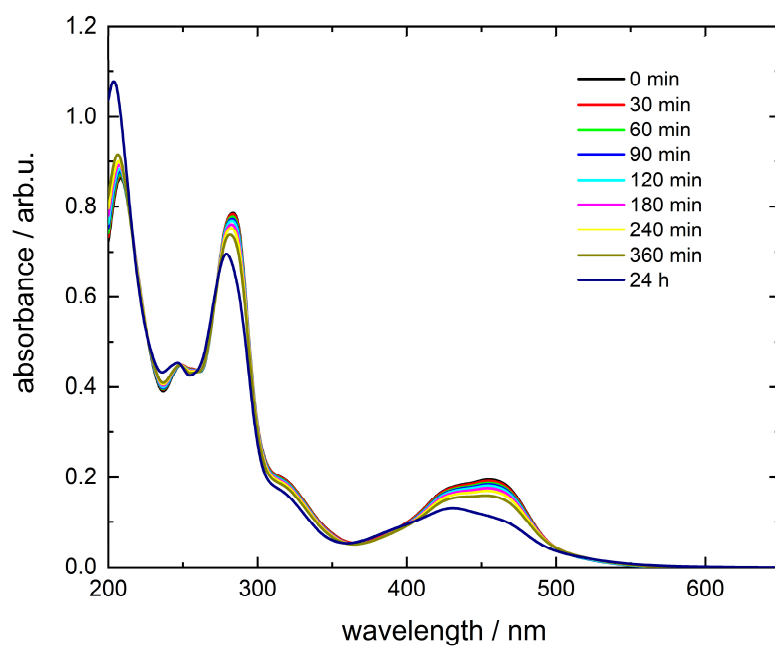
## 5.4 Photochemical characterization



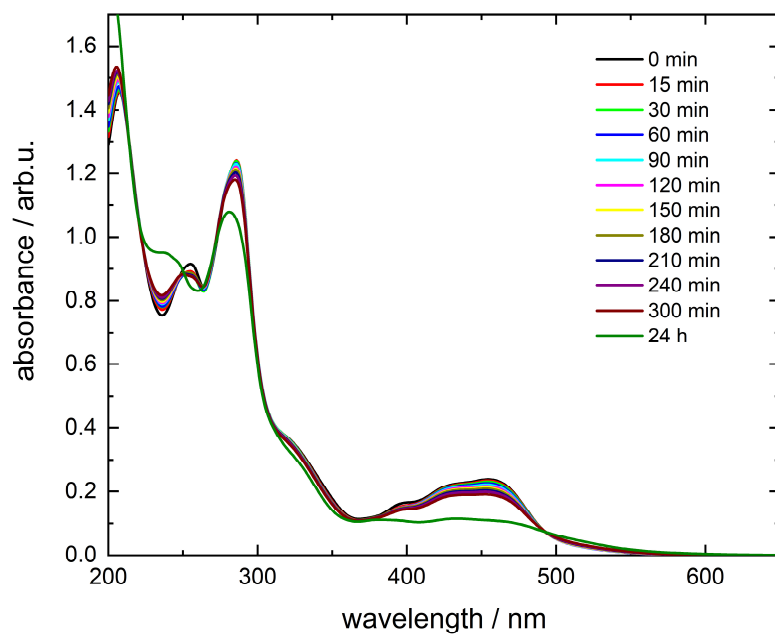
**Figure S15.** Photostability measurements of 7.5 mL of a  $1 \cdot 10^{-5}$  M Ru-solution in aerated acetonitrile irradiated with two LED-stick ( $2 \times 470 \pm 20$  nm,  $45 \pm 5$  mW·cm $^{-2}$ ) under air cooling. The samples were irradiated in a 21 mL schlenk tube equipped with a septum on the top. In case of mercury addition, the suspension was vigorously stirred.



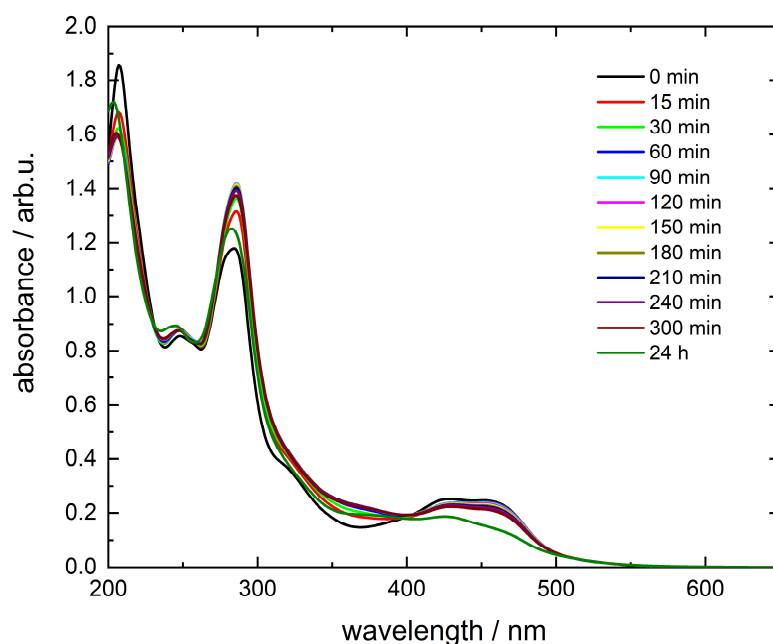
**Figure S16.** Photostability measurements of  $1 \cdot 10^{-5}$  M **Rup(ph)p** in aerated acetonitrile irradiated with one LED-stick ( $470 \pm 20$  nm,  $45 \pm 5$  mW·cm $^{-2}$ ) under air cooling.



**Figure S17.** Photostability measurements of  $1 \cdot 10^{-5}$  M **Rup(ph)pRu** in aerated acetonitrile irradiated with one LED-stick ( $470 \pm 20$  nm,  $45 \pm 5$  mW·cm<sup>-2</sup>) under air cooling.



**Figure S18.** Photostability measurements of  $1 \cdot 10^{-5}$  M **Rup(ph)pPtCl<sub>2</sub>** in aerated acetonitrile irradiated with one LED-stick ( $470 \pm 20$  nm,  $45 \pm 5$  mW·cm<sup>-2</sup>) under air cooling.

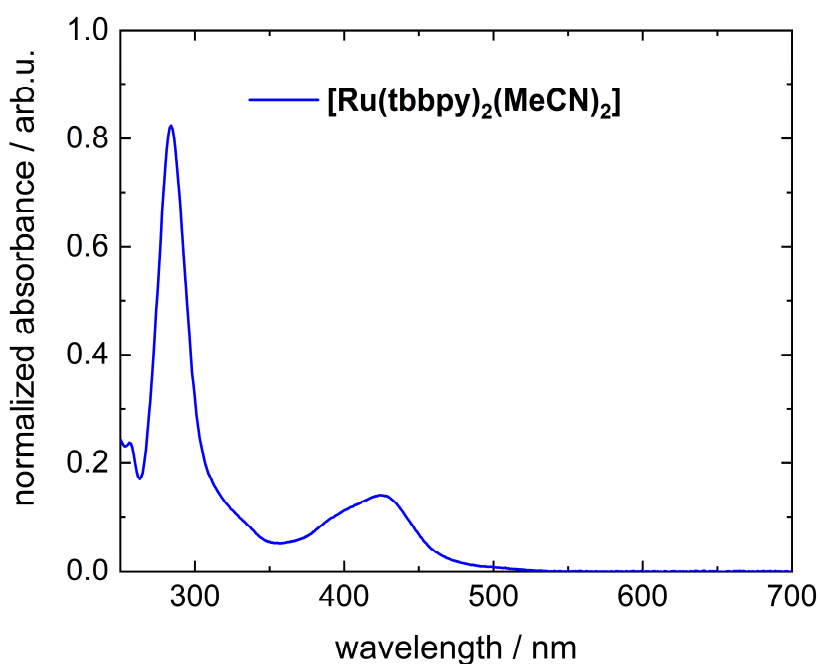


**Figure S19.** Photostability measurements of  $1 \cdot 10^{-5}$  M **Rup(ph)pPtI<sub>2</sub>** in aerated acetonitrile irradiated with one LED-stick ( $470 \pm 20$  nm,  $45 \pm 5$  mW·cm<sup>-2</sup>) under air cooling.

**Table S1.** Photostabilities as percentage of Ru-complexes in air-saturated acetonitrile after different time intervals of irradiation with one LED-stick ( $470 \pm 20$  nm,  $45$  mW  $\pm$  5 mW·cm<sup>-2</sup>) under air cooling.

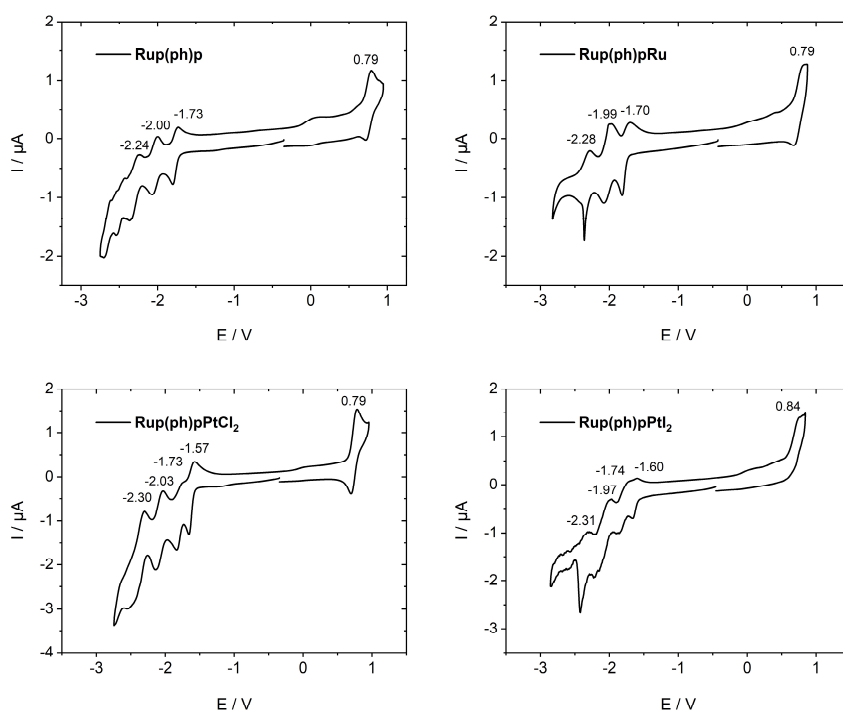
time	Rup(ph)p <sup>[a]</sup>	Rup(ph)pRu <sup>[a]</sup>	Rup(ph)pPtCl <sub>2</sub> <sup>[a]</sup>	Rup(ph)pPtI <sub>2</sub> <sup>[a]</sup>
0 min	0	0	0	0
30 min	2.9	1.6	3.4	2.4
60 min	5.4	4.1	5.6	2.6
90 min	7.8	5.8	7.6	3.5
120 min	10.1	7.4	9.7	5.0
180 min	14.2	10.2	13.0	8.0
240 min	18.7	13.4	17.2	11.3
<b>24 h</b>	<b>62.9</b>	<b>44.0</b>	<b>54.1</b>	<b>41.6</b>

<sup>[a]</sup> At 460 nm the loss of absorption was the maximum, while the possible photolyzed product [Ru(tbbpy)<sub>2</sub>(MeCN)<sub>2</sub>] provided a negligible absorption (Figure S18). We therefore used this wavelength to determine the value of the absorption. The percentual decrease of absorption was calculated against the absorption intensity before irradiation as the reference.



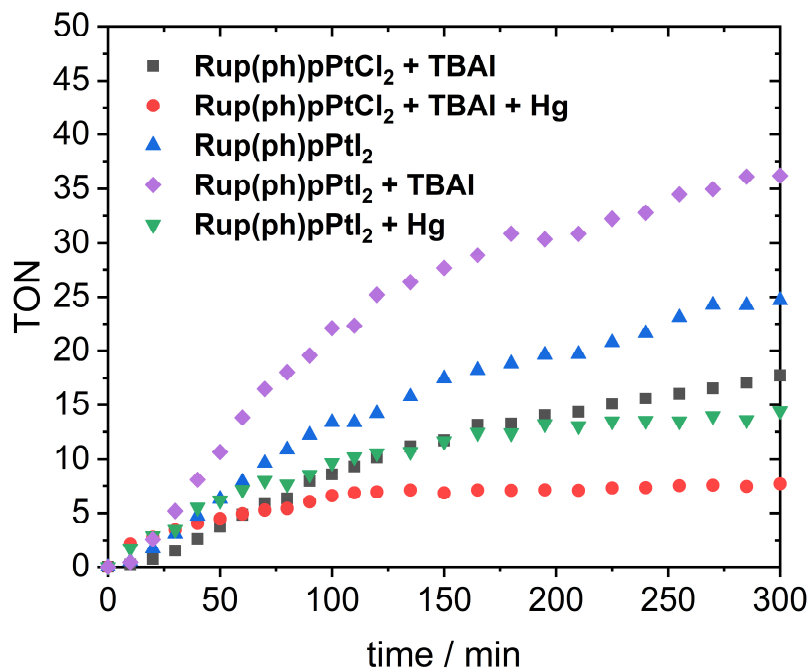
**Figure S20.** Absorption spectrum of  $[\text{Ru}(\text{tbbpy})_2(\text{MeCN})_2](\text{PF}_6)_2$ , representing a putative degradation product of the photolysis of **Rup(ph)p**-type complexes in acetonitrile. As the absorption at 460 nm is low, we used this wavelength to calculate the photostabilities for all **Rup(ph)p**-type complexes.

## 5.5 Electrochemical characterization

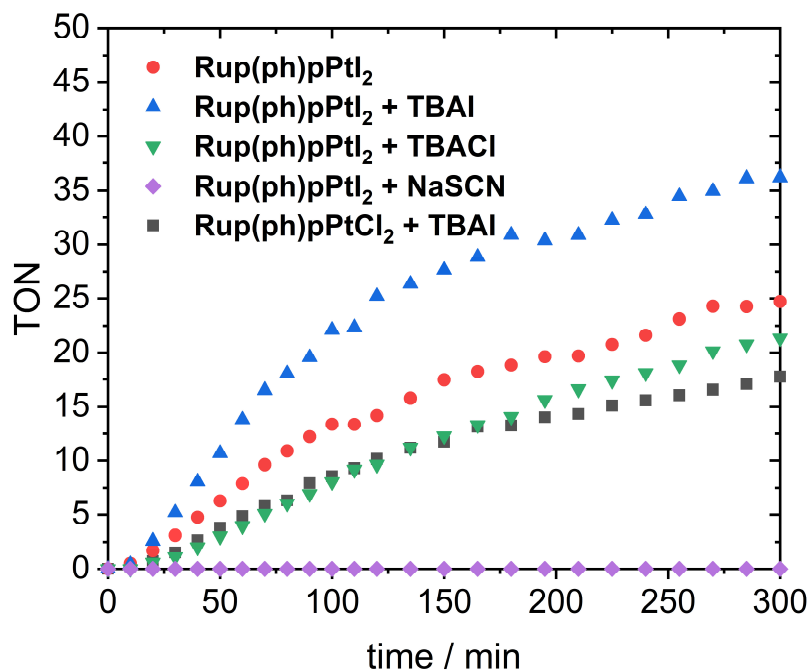


**Figure S21.** Cyclic voltammogram of the Ru-complexes recorded in deaerated acetonitrile. Ferrocene/Ferrocenium ( $\text{Fc}/\text{Fc}^+ = 0.00 \text{ V}$ ) was used as internal standard. Tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6 = 0.1 \text{ M}$ ) was used as supporting electrolyte. The values marked in the CV represent the oxidation waves. The wave at approx. 0.4 to 0.5 V can be assigned to artefacts generated by the electrode (e.g. due to deposits).

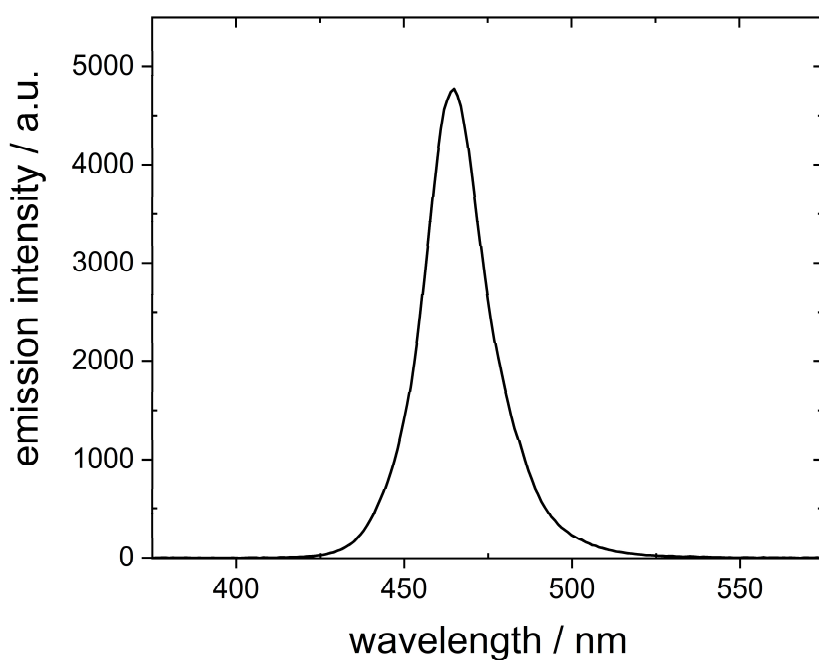
## 5.6 Catalysis



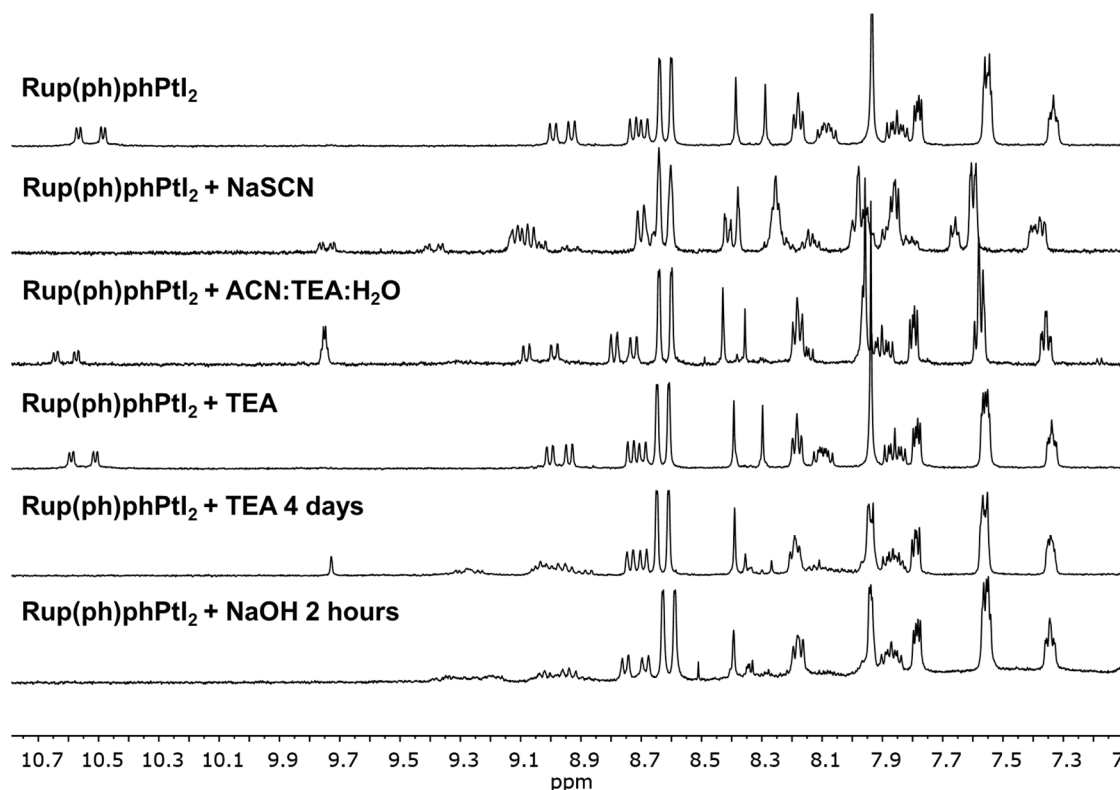
**Figure S22.** Photocatalytic hydrogen evolution by  $\text{Rup(ph)pPtCl}_2$  and  $\text{Rup(ph)pPtI}_2$  with/without addition of 200 eq. TBAI and/or mercury to a  $70 \mu\text{M}$  ( $V = 7.5 \text{ mL}$ ) complex solution irradiated with two LED-sticks ( $470 \pm 20 \text{ nm}$ ,  $45 \pm 5 \text{ mW}\cdot\text{cm}^{-2}$ ). The amount of produced hydrogen was quantified by GC-TCD-determination of the headspace ( $50 \mu\text{L}$  aliquots).



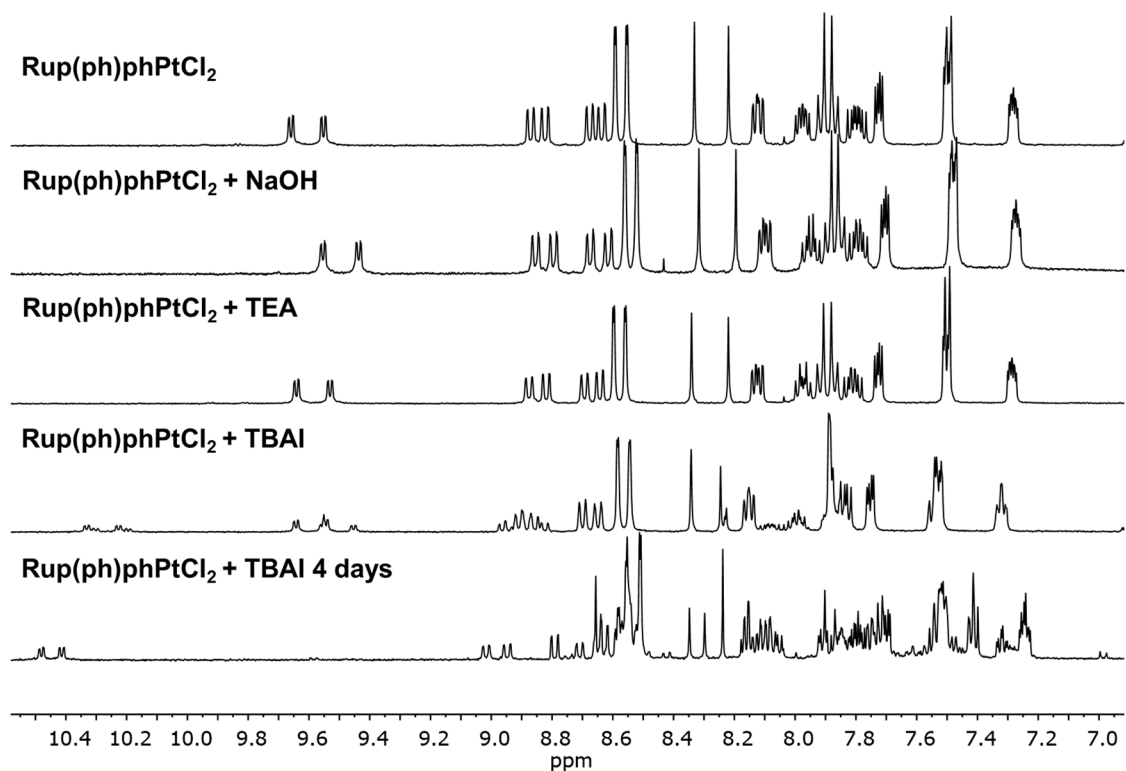
**Figure S23.** Photocatalytic hydrogen evolution by  $\text{Rup(ph)pPtCl}_2$  and  $\text{Rup(ph)pPtI}_2$  with addition of 200 eq. TBAI/TBACl/NaSCN to a  $70 \mu\text{M}$  ( $V = 7.5 \text{ mL}$ ) complex solution irradiated with two LED-sticks ( $470 \pm 20 \text{ nm}$ ,  $45 \pm 5 \text{ mW}\cdot\text{cm}^{-2}$ ). The amount of produced hydrogen was quantified by GC-TCD-determination of the headspace ( $50 \mu\text{L}$  aliquots).



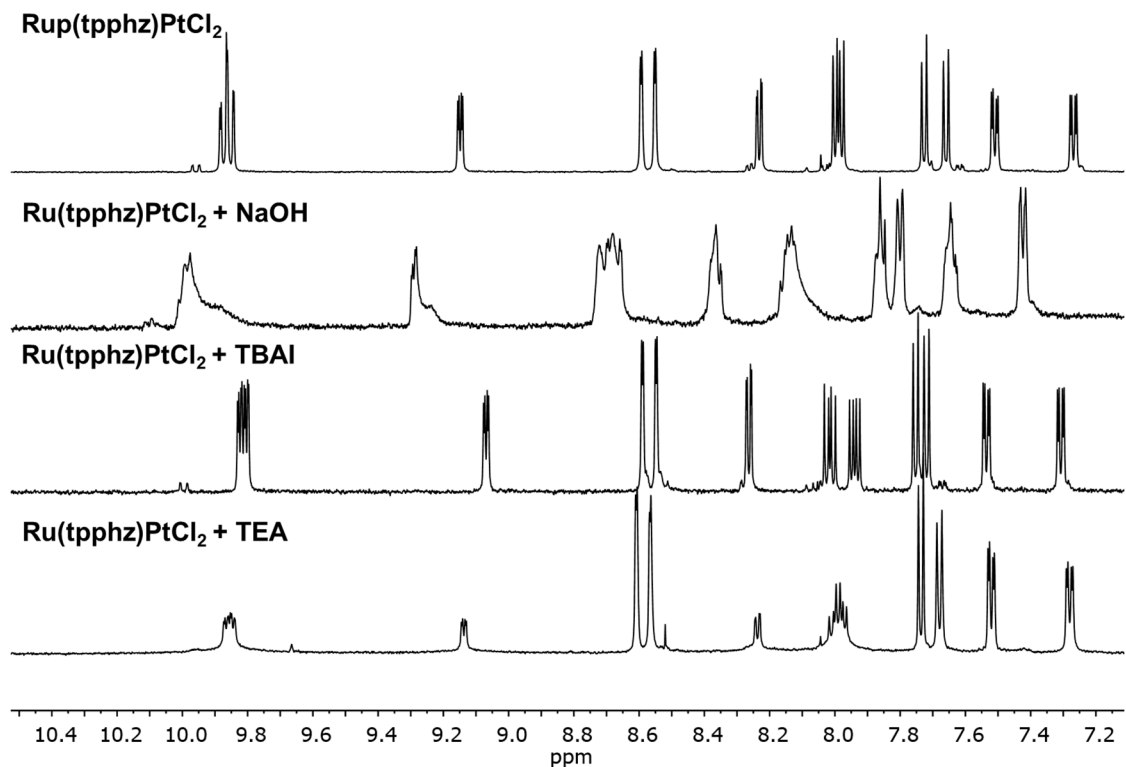
**Figure S24.** Typical emission profile of the utilized LED-sticks for irradiation during catalysis. Maximum emission at 465 nm (4770 a.u.). 50% of maximum emission at 454 nm and 477 nm (i.e. FWHM of 23 nm).



**Figure S25.**  $^1\text{H}$  NMR of **Rup(ph)pPtI<sub>2</sub>** (1<sup>st</sup>) and with addition of NaSCN (2<sup>nd</sup>), 6:3:1 (v:v:v) ACN:TEA:H<sub>2</sub>O (3<sup>rd</sup>), triethylamine (4<sup>th</sup>) and after 4 days (5<sup>th</sup>) and with NaOH (6<sup>th</sup>) in 2:1 methanol:acetonitrile at room temperature. Interestingly, addition of NaSCN exchanges the iodide ligands at the Pt-centre whereas triethylamine has at the beginning no influence. However, after four days significant changes at the CC reflect the instability of **Rup(ph)pPtI<sub>2</sub>** towards bases. This is also visible *via* NaOH addition. It is tempting to speculate whether a triethylamine stabilized intermediate is formed, indicated by the formation of a signal at approx. 9.70 ppm under catalytic conditions.

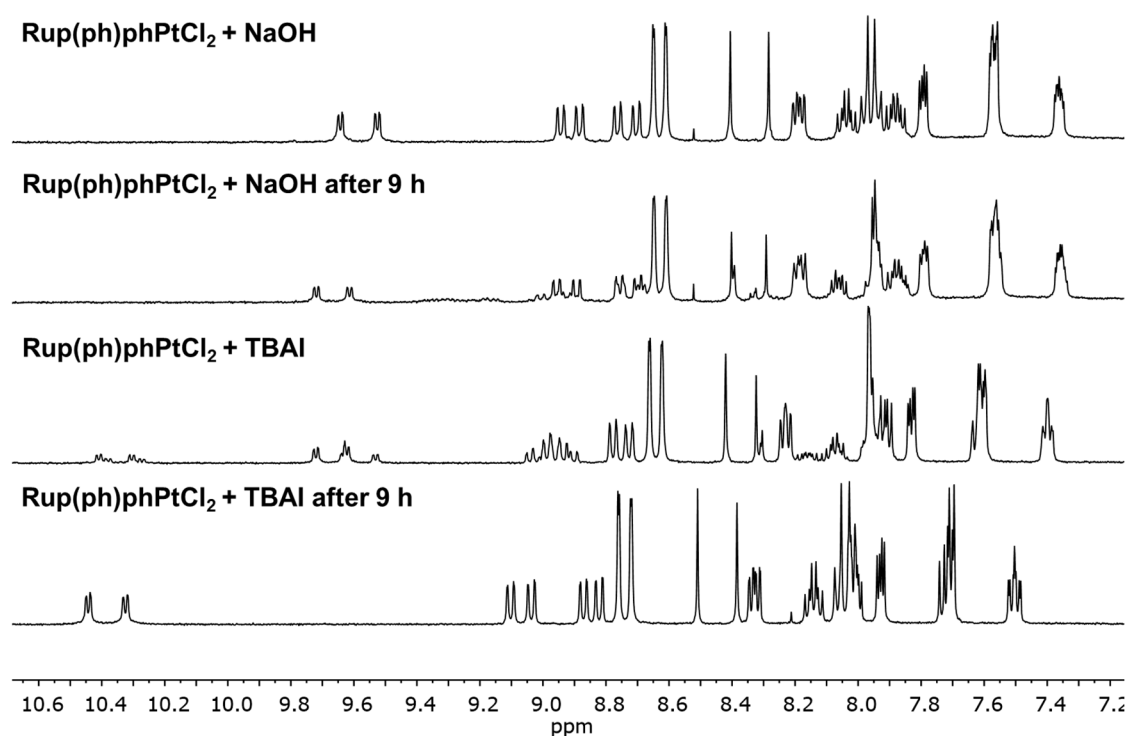


**Figure S26.**  $^1\text{H}$  NMR of  $\text{Rup}(\text{ph})\text{phPtCl}_2$  (1<sup>st</sup>) and with addition of NaOH (2<sup>nd</sup>), triethylamine (3<sup>rd</sup>), TBAI (4<sup>th</sup>) and with TBAI after four days (5<sup>th</sup>) in 2:1 methanol:acetonitrile at room temperature. Interestingly, addition of TBAI causes exchange of the halide ligands at the Pt-centre (shift of the 2',9'-protons from ca. 9.80 ppm to 10.50 ppm). However, in this case the addition of triethylamine (bottom) has no influence on the CC at all.

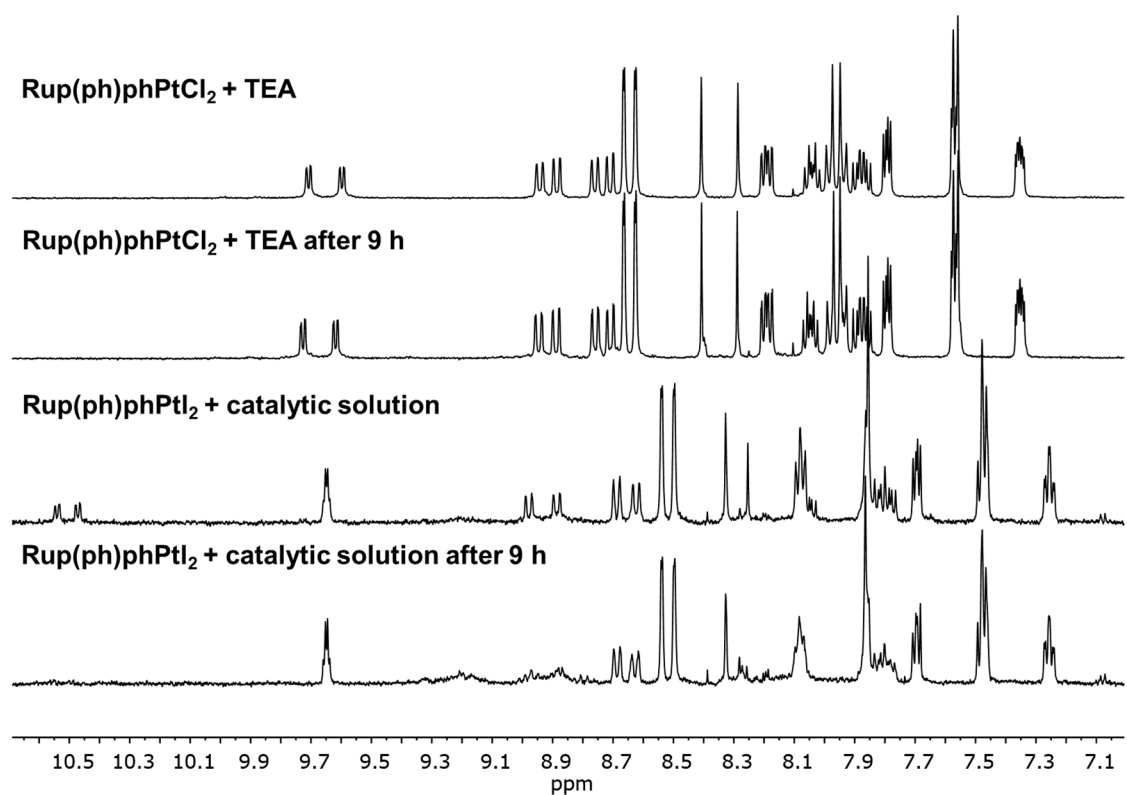


**Figure S27.**  $^1\text{H}$  NMR of  $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})\text{PtCl}_2](\text{PF}_6)_2$  (1<sup>st</sup>) and with addition of NaOH (2<sup>nd</sup>), TBAI (3<sup>rd</sup>) and triethylamine (4<sup>th</sup>) in 2:1 methanol:acetonitrile at room temperature. Interestingly, addition of TBAI causes no exchange of the halide ligands at the Pt-centre. However, slightly shifts are observed due to stacking and ion concentration effects.

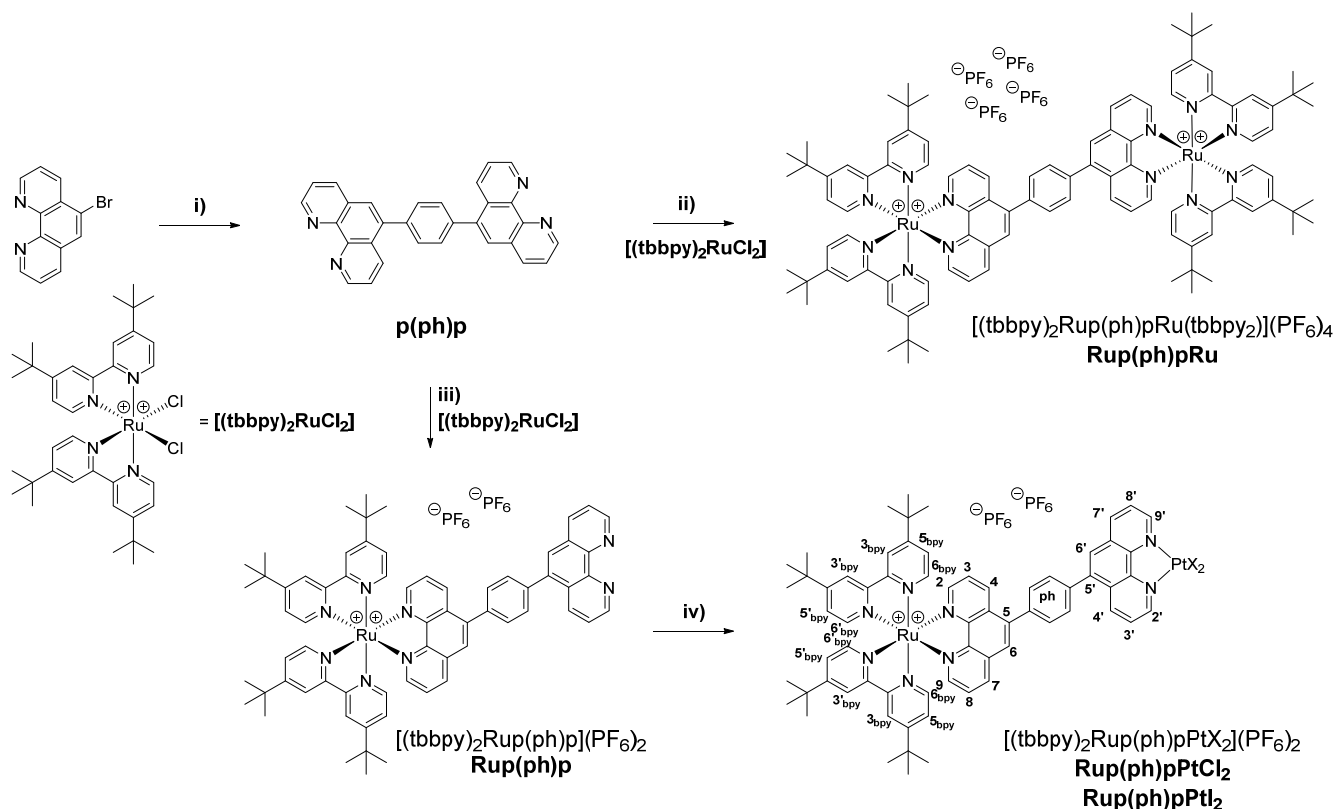




**Figure S28.**  $^1\text{H}$  NMR of  $\text{Rup(ph)pPtCl}_2$  and with addition of NaOH (1<sup>st</sup>) and after 9 h (2<sup>nd</sup>) and with addition of TBAI (3<sup>rd</sup>) and after 9 h (4<sup>th</sup>). Decomposition in case of NaOH addition after 9 h as well as complete Cl-I ligand exchange at the CC was observed.



**Figure S29.**  $^1\text{H}$  NMR of  $\text{Rup(ph)pPtCl}_2$  and with addition of TEA (1<sup>st</sup>) and after 9 h (2<sup>nd</sup>) in 2:1 methanol:acetonitrile and of  $\text{Rup(ph)pPtI}_2$  in 6:3:1 acetonitrile:TEA:H<sub>2</sub>O (v:v:v) (3<sup>rd</sup>) and after 9 h (4<sup>th</sup>). Interestingly,  $\text{Rup(ph)pPtI}_2$  decomposed completely within the course of 9 h.



**Scheme S1.** Molecular structure, <sup>1</sup>H NMR assignment and synthetic access to mono- and dinuclear ruthenium complexes of 5,5'-linked, phenyl-spaced bis-phenanthroline bridging ligands. i) 1,4-bis(4,4,4-tetramethyl-1,2,3-dioxoborolan-2-yl)benzene, Pd(PPh<sub>3</sub>)Cl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, DMSO, 100°C, 48-72 h; yield: 71%; ii) [(tbbpy)<sub>2</sub>RuCl<sub>2</sub>], ethanol/ethylene glycol (v:v = 1:1), 130°C, 3.5 h; yield: 89%; iii) [(tbbpy)<sub>2</sub>RuCl<sub>2</sub>], ethanol/ethylene glycol (v:v = 1:1), 130°C, 3.5 h; yield: 63.8%; iv) [Pt(DMSO)<sub>2</sub>X<sub>2</sub>] (X = Cl, I), ethanol, reflux, 5 h; yield: 85-88%.

## 6. References

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