

Electronic Supplementary Information

Iridium(III) molecular catalysts for water oxidation: the simpler the faster

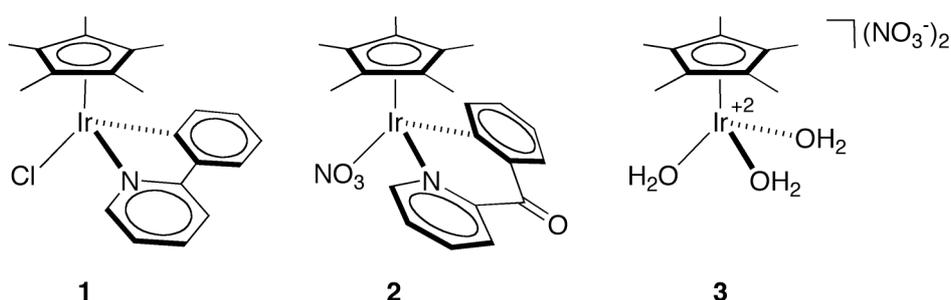
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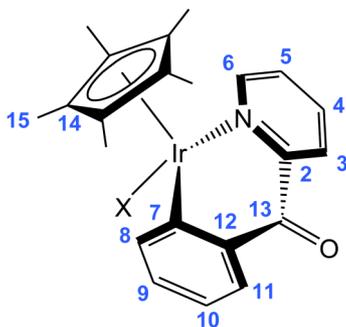
$[\text{Cp}^*\text{Ir}(\mu\text{-Cl})\text{Cl}]_2$,¹ $[\text{Cp}^*\text{Ir}(\text{ppy})\text{Cl}]$ (ppy = 2-phenylpyridine, **1**)² and $[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3](\text{NO}_3)_2$ (**3**)³ were synthesized according to the procedures reported in the literature. AgNO_3 (Fluka), ppy (Sigma-Aldrich), 2-benzoylpyridine (Sigma-Aldrich) and $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (Alfa Aesar) were purchased and used without any further purification.

All compounds were characterized in solution by recording ^1H - and ^{13}C -NMR one- and two-dimensional ^1H and ^{13}C NMR spectra on a Bruker DRX 400 spectrometer. Referencing is relative to TMS (^1H and ^{13}C).



Scheme 1. Catalysts for water oxidation

Synthesis of $[(\text{Cp}^*)\text{Ir}(2\text{-bzpy})\text{NO}_3]$ (2**).** 100 mg of $[\text{Cp}^*\text{Ir}(\mu\text{-Cl})\text{Cl}]_2$, 2.2 equivalents of 2-benzoylpyridine and 3 equivalents of NaCH_3COO were dissolved in 5 mL of CH_2Cl_2 . The solution was warmed up and left under reflux for 24h. The volatiles were removed under reduced pressure and the resulting solid washed three times with a 1:4 ethyl ether/n-hexane solution and one with n-hexane (10 mL). The resulting solid was dried obtaining $[(\text{Cp}^*)\text{Ir}(2\text{-bzpy})\text{Cl}]$ (**4**) in almost quantitative yield. Compound **4** was found to be insoluble in water. Its suspension in water was reacted with an equimolar amount of AgNO_3 at room temperature. AgCl precipitated from the solution and was filtered off. The resulting solution was extracted with CH_2Cl_2 obtaining, after some work up, compound **2** in 60% yield. Crystals of **2** suitable for X-Ray single crystal study were obtained from a slow diffusion of n-hexane in a solution of **2** in CH_2Cl_2 (n-hexane/ CH_2Cl_2 7/1 in volume).



Scheme 2. Numbering of protons and carbons (X = Cl or NO₃)

Characterization of **4**. ¹H-NMR (CD₂Cl₂, 298K): δ 9.07 (ddd, H6, ³J_{H6,H5}=5.67 Hz, ⁴J_{H6,H4}=1.54 Hz, ⁵J_{H6,H3}=0.66 Hz); 8.13 (ddd, H3, ³J_{H3,H4}=7.91 Hz, ⁴J_{H3,H5}=1.58 Hz); 7.89 (ddd, H4, ³J_{H4,H5}≈³J_{H4,H3}); 7.78 (dd, H11, ³J_{H11,H10}=7.75 Hz, ⁴J_{H11,H9}=1.48 Hz); δ 7.74 (dd, H8, ³J_{H8,H9}=7.46 Hz, ⁴J_{H8,H10}=1.14 Hz); 7.42 (ddd, H5); 7.22 (ddd, H9, ³J_{H9,H8}≈³J_{H9,H10}); 7.00 (ddd, H10); 1.34 (s, H15). ¹³C-NMR (CD₂Cl₂, 298K): δ 192.42 (s, C13); 157.31 (s, C12); 156.90 (s, C2); 156.46 (s, C6); 141.25 (s, C8); 138.67 (s, C4); 137.95 (s, C7); 132.39 (s, C9); 128.12 (s, C11); 128.00 (s, C5); 125.47 (s, C3); 123.54 (s, C10); 89, 64 (s, C14); 8.57 (s, C15). Anal. Calcd. for C₂₂H₂₃ClIrNO: C, 48.48; H, 4.25; N, 2.57. Found: C, 48.62; H, 4.41; N, 2.38.

Characterization of **2**. ¹H-NMR (CD₂Cl₂, 298K): δ 9.23 (dd, H6, ³J_{H6,H5}=5.65 Hz, ⁴J_{H6,H4}=1.46 Hz); 8.22 (dd, H3, ³J_{H3,H4}=7.92 Hz, ⁴J_{H3,H5}=1.55 Hz); 7.96 (ddd, H4, ³J_{H4,H5}=7.78 Hz, ⁴J_{H4,H6}=1.59 Hz); 7.91 (dd, H11, ³J_{H11,H10}=7.74 Hz, ⁴J_{H11,H9}=1.09 Hz); δ 7.83 (dd, H8, ³J_{H8,H9}=7.74 Hz, ⁴J_{H8,H10}=1.55 Hz); 7.53 (ddd, H5, ³J=7.45 Hz, ⁴J_{H5,H3}=1.63 Hz); 7.30 (ddd, H9, ³J=7.39 Hz, ⁴J_{H9,H11}=1.57 Hz); 7.00 (ddd, H10, ³J=7.98 Hz, ⁴J_{H10,H8}=1.18 Hz), 1.32 (s, H15). ¹³C-NMR (CD₂Cl₂, 298K): δ 192.46 (s, C13); 157.42 (s, C12); 156.21 (s, C2); 155.73 (s, C6); 139.54 (s, C8); 139.13 (s, C4); 137.21 (s, C7); 132.99 (s, C9); 128.84 (s, C11); 128.60 (s, C5); 126.45 (s, C3); 124.43 (s, C10); 84.55 (s, C14); 9.02 (s, C15). Anal. Calcd. for C₂₂H₂₃IrN₂O₄: C, 46.22; H, 4.06; N, 4.90. Found: C, 46.43; H, 4.11; N, 4.67.

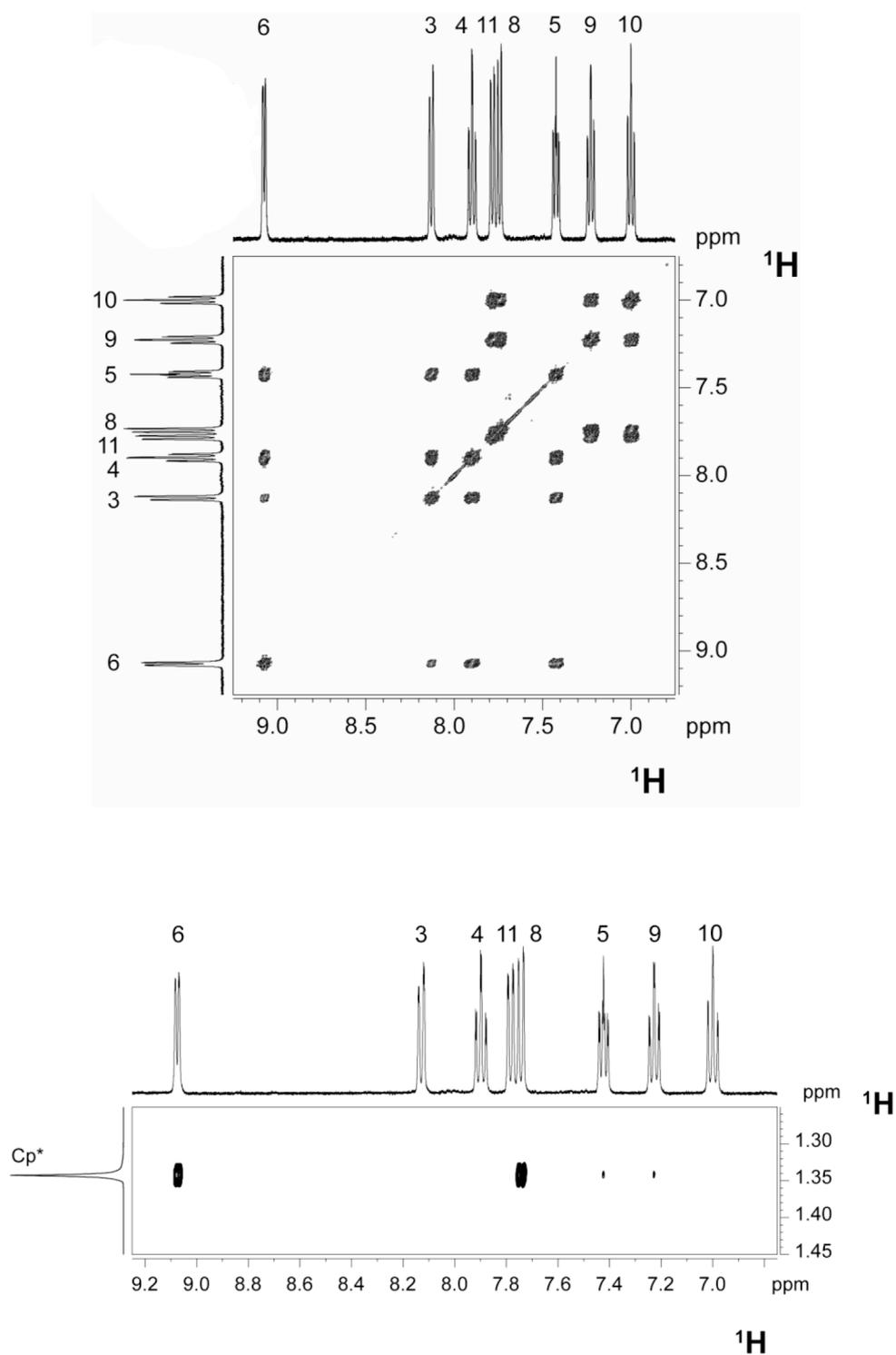


Figure 1. Sections of ^1H NOESY (down) and ^1H COSY (up) NMR spectra of compound **4** (400.13 MHz, CD_2Cl_2 , 296 K)

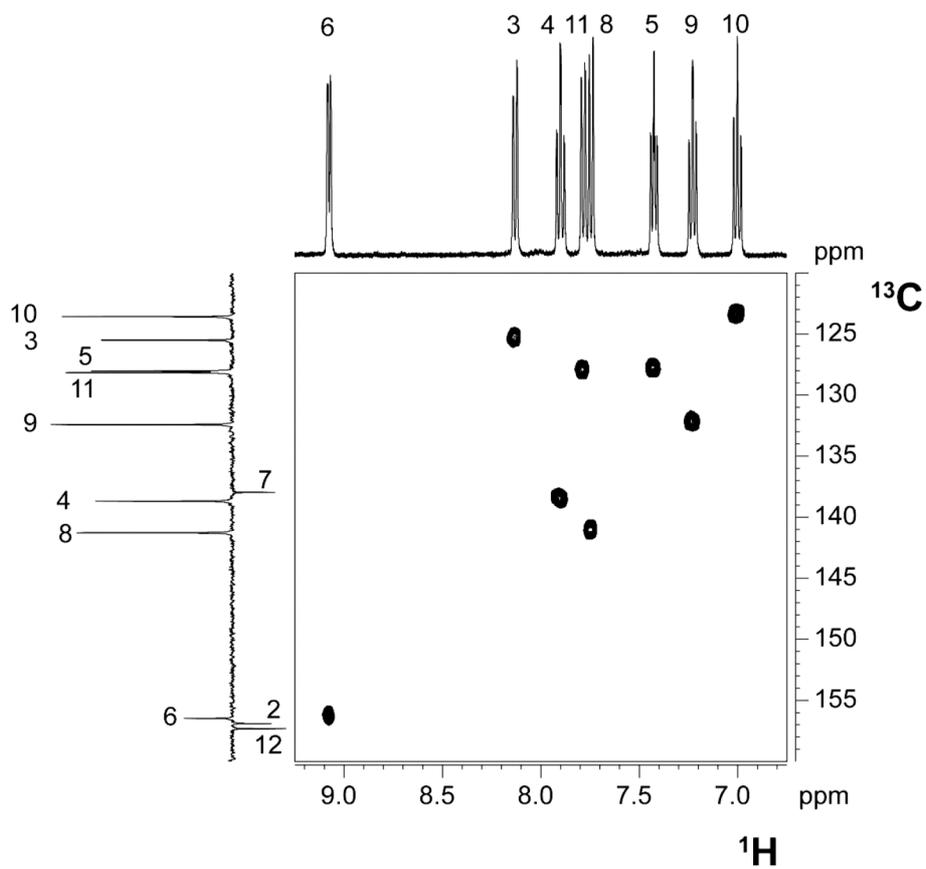


Figure 2. A section of the $^1\text{H}^{13}\text{C}$ -HMQC NMR spectrum of compound **4** (400.13 MHz, CD_2Cl_2 , 296 K)

Kinetic Measurements. Experiments were performed at pH =1 (HNO₃ 0.1 M) and 25°C on a Beckman UV-Vis diode array spectrophotometer (DU 7500) by monitoring the disappearance of Ce⁴⁺ [Cerium(IV) ammonium nitrate (CAN), (NH₄)₂Ce(NO₃)₆] at 340 nm. The concentration of **1-3** compounds ranged from 2 x10⁻⁷ M to 5 x 10⁻⁶ M; the concentration of CAN was ca. 1 x 10⁻³ M. In a typical experiment, about 5 mg of catalyst was weighted on a precision balance (± 1 µg) and dissolved in 250 mL of a solution 0.1M of HNO₃ in water obtaining a ca. 10⁻⁵ M catalyst solution. A suitable amount of the latter was withdrawn and diluted in order to obtain the desired catalyst concentration (Table S1). 1.5 mL of the catalyst solution were introduced in the cuvette of the UV-Vis spectrophotometer, interfaced with a thermostat, and left for 20 min until the temperature reached the constant value of 25°C. 1.5 mL of a ca. 2 x 10⁻³ M solution of CAN (0.0110 ± 0.0001 g in 10 mL) in 0.1 M of HNO₃, previously thermostated at 25°C, were introduced in the cuvette and the data acquisition was started. The absorbance at 340 nm was read every 20 s. Each kinetic experiment was replicate at least twice.

Table 1. Kinetic data for compounds **1-3**.

Compound	Conc. (μM)	$k_{\text{obs}} \times 10^7 (\text{M s}^{-1})$
1	0.43	0.31
	1.07	0.94
	2.60	2.53
	5.40	4.20
2	0.21	0.21
	0.21	0.32
	0.42	0.66
	1.07	1.52
	1.08	1.43
	2.58	3.64
	5.33	7.51
3	0.21	0.25
	1.07	2.24
	2.60	7.45
	5.30	13.37

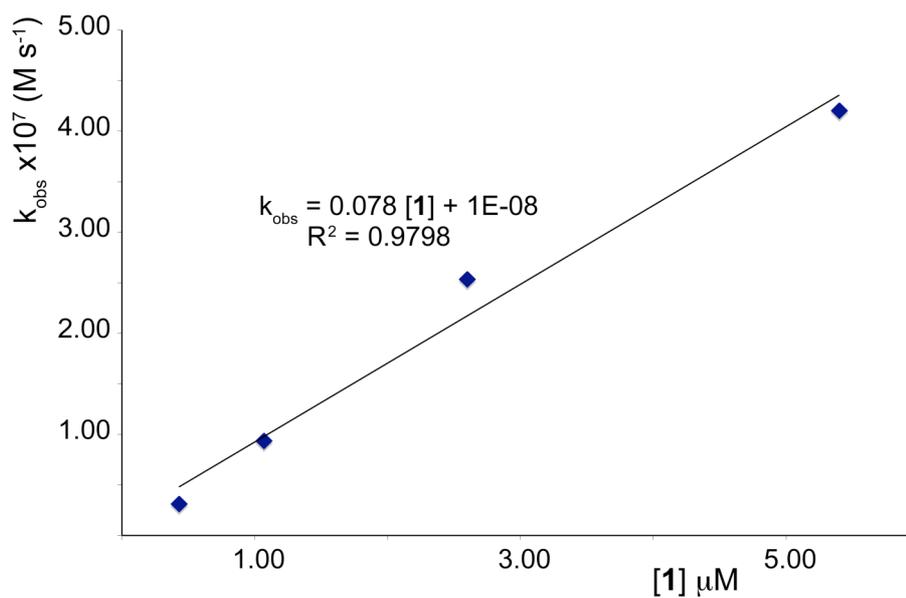


Figure 3. Plot of zeroth-order rate constants in Ce(IV) (k_{obs}) versus the concentration of **1**

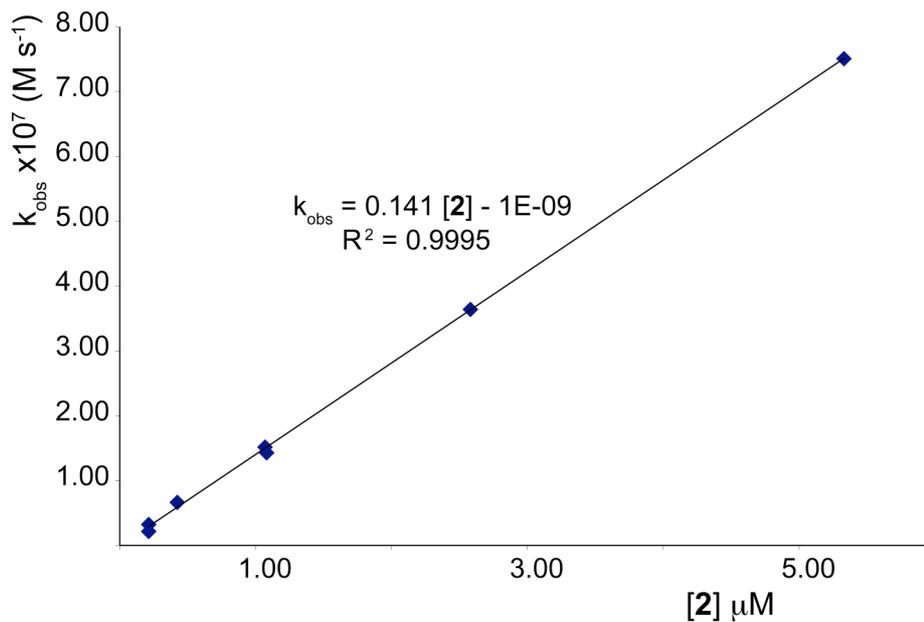


Figure 4. Plot of zeroth-order rate constants in Ce(IV) (k_{obs}) *versus* the concentration of **2**

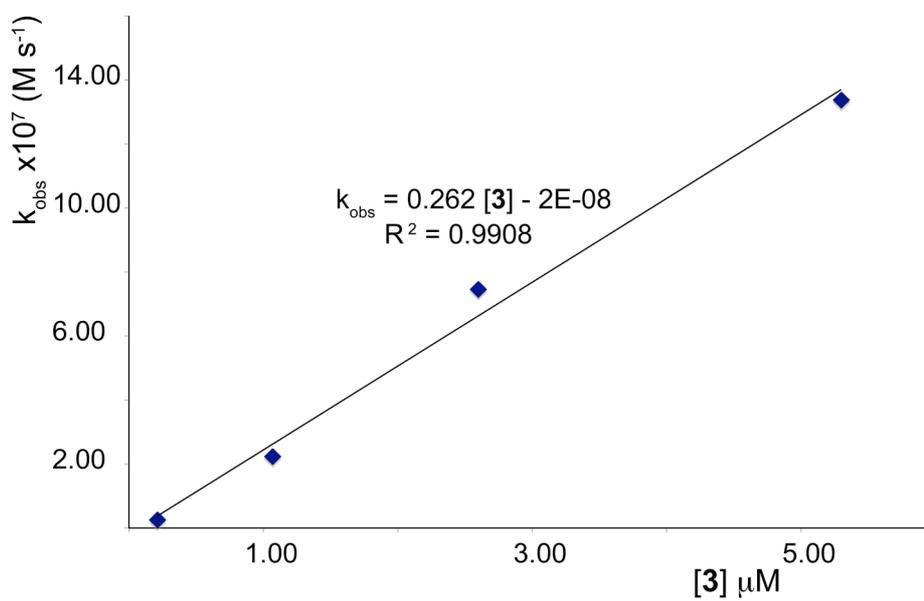


Figure 5. Plot of zeroth-order rate constants in Ce(IV) (k_{obs}) *versus* the concentration of **3**

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