Supporting Information

Oxygen Reduction Mechanism of Monometallic Rhodium Hydride Complexes

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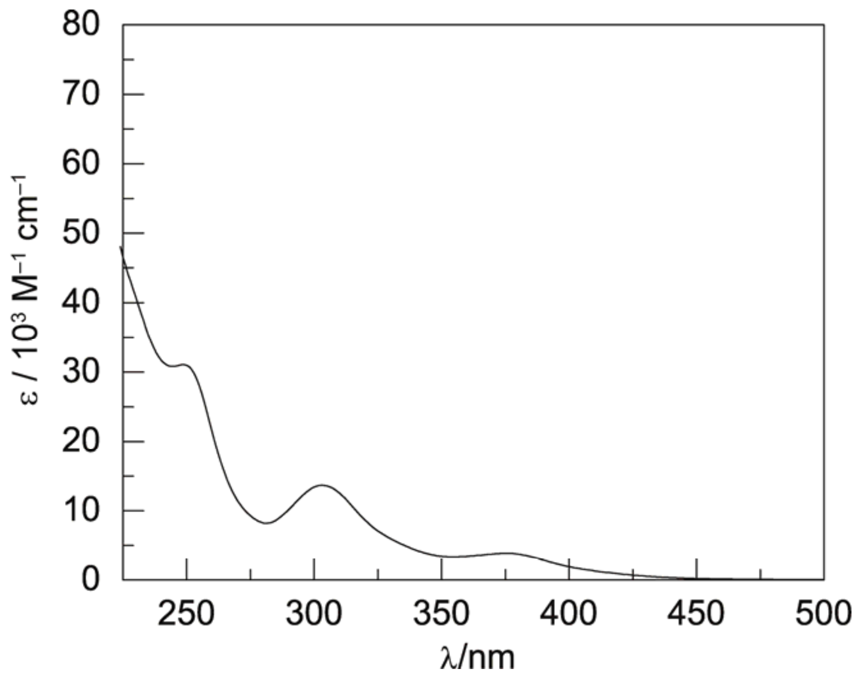

Figure S1. Electronic absorption spectrum of **1a** recorded at 293 K in THF.

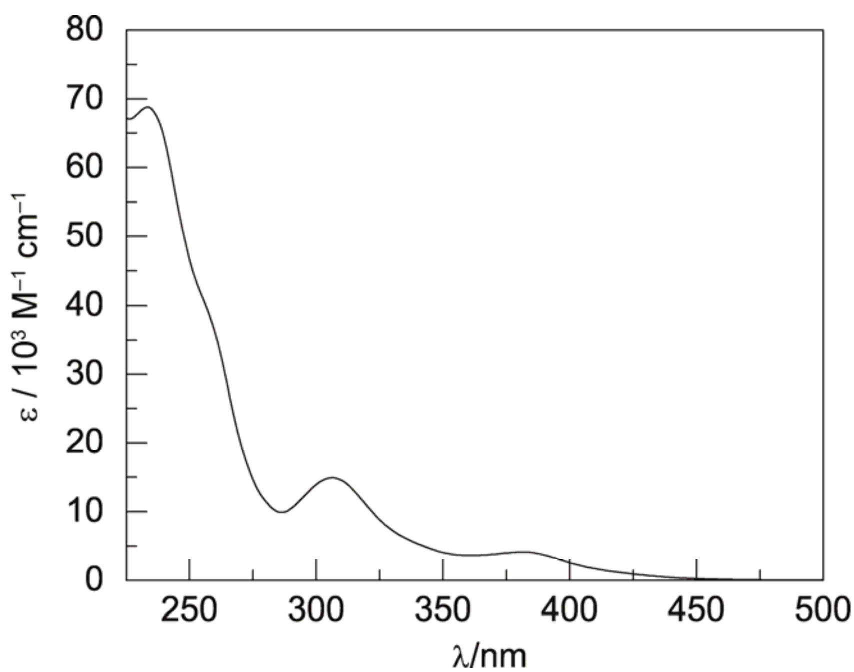

Figure S2. Electronic absorption spectrum of **1b** recorded at 293 K in THF.

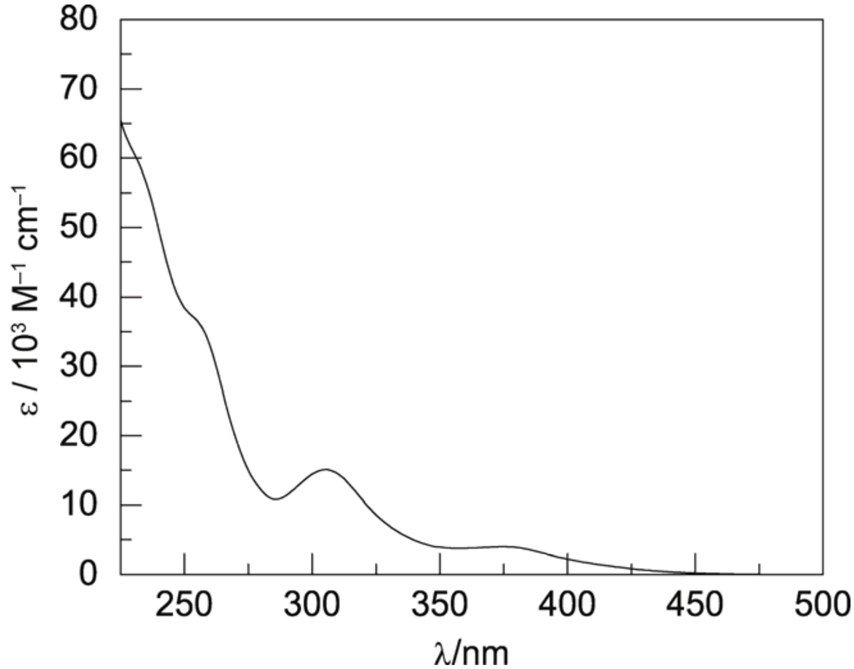

Figure S3. Electronic absorption spectrum of **1c** recorded at 293 K in THF.

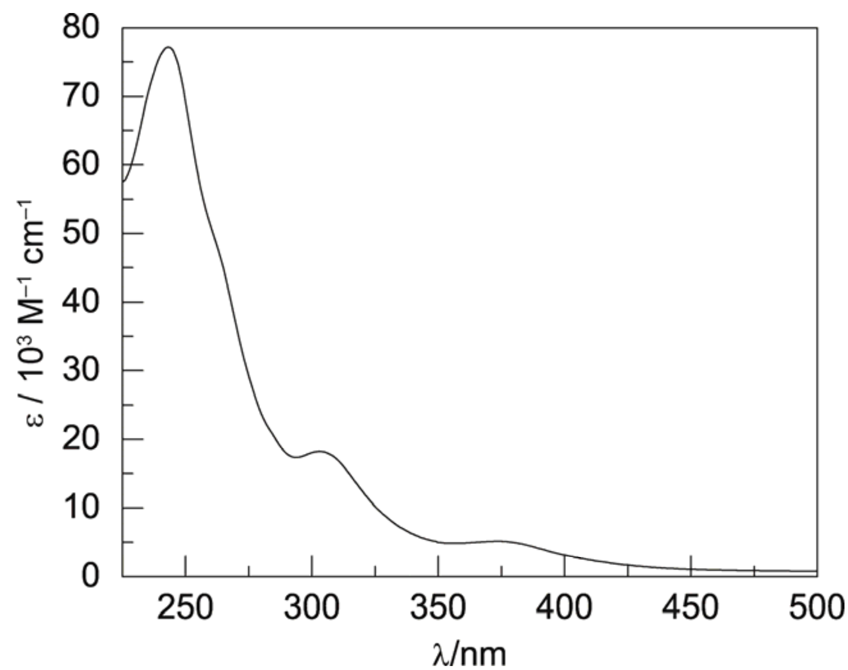

Figure S4. Electronic absorption spectrum of **1d** recorded at 293 K in THF.

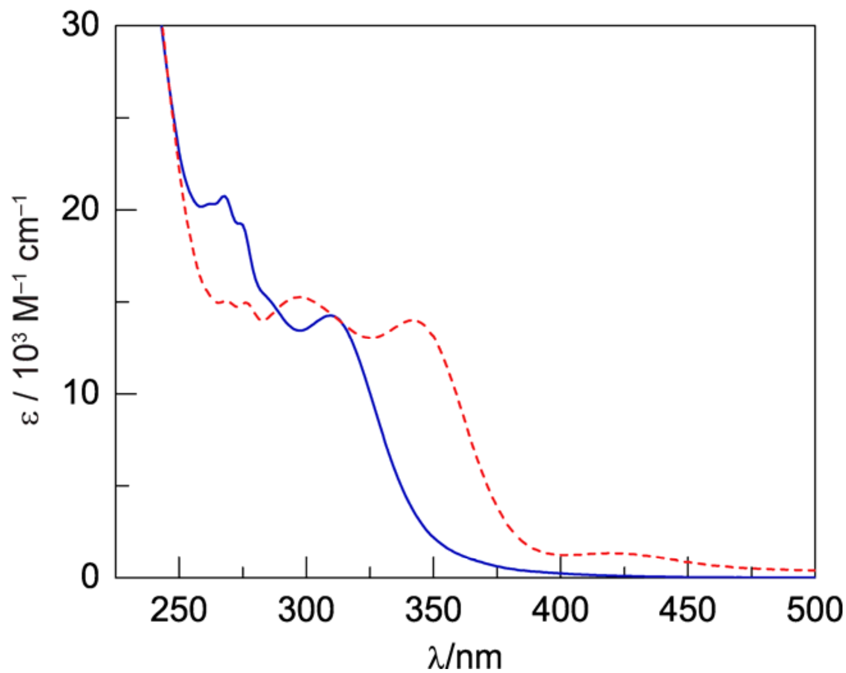

Figure S5. Overlaid electronic absorption spectra of **2a** (▬) and **3a** (‒ ‒) recorded at 293 K in THF.

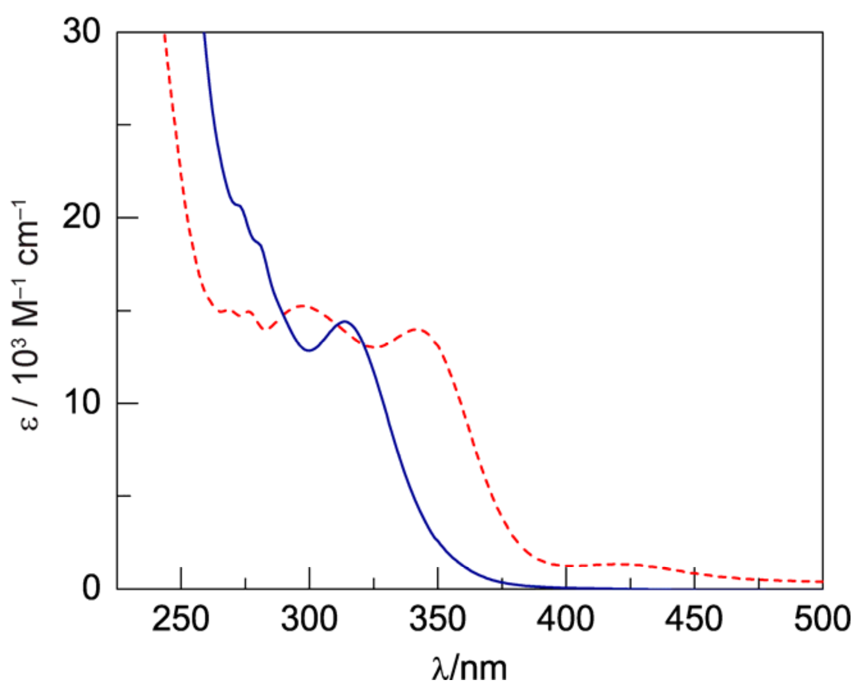

Figure S6. Overlaid electronic absorption spectra of **2b** (▬) and **3b** (‒ ‒) recorded at 293 K in THF.

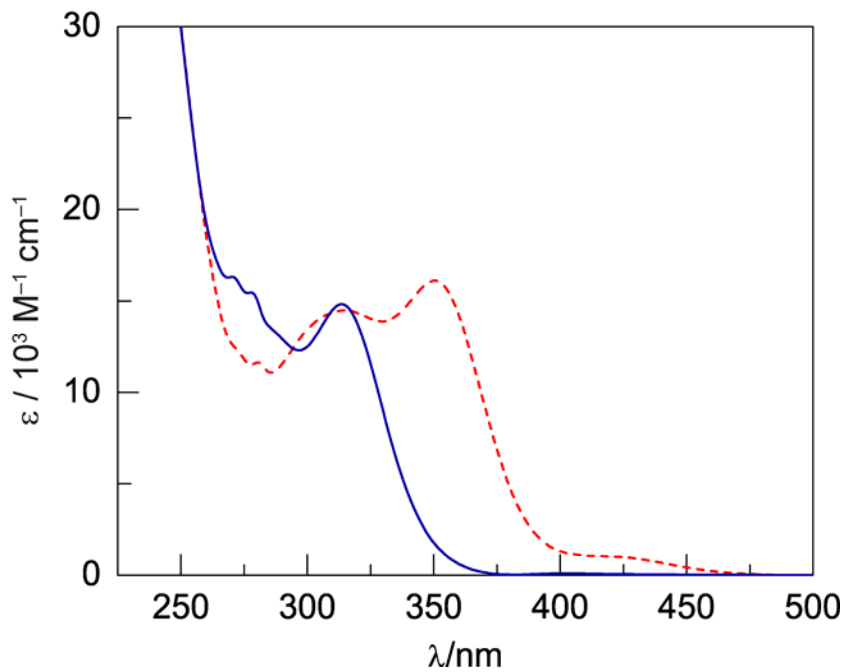

Figure S7. Overlaid electronic absorption spectra of **2c** (▬▬) and **3c** (▬ ▬) recorded at 293 K in THF.

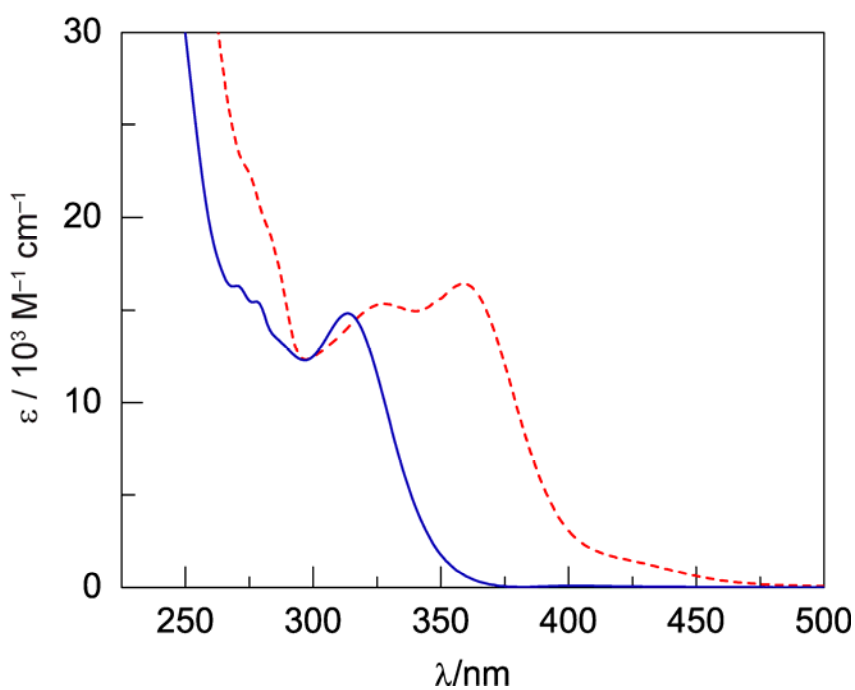

Figure S8. Overlaid electronic absorption spectra of **2d** (▬▬) and **3d** (▬ ▬) recorded at 293 K in THF.

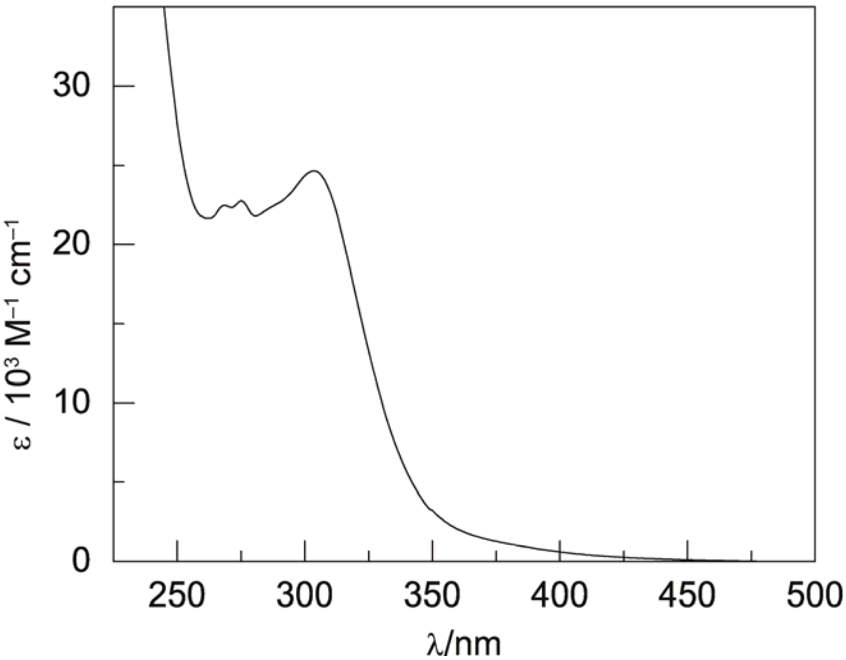

Figure S9. Electronic absorption spectrum of **4a** recorded at 293 K in THF.

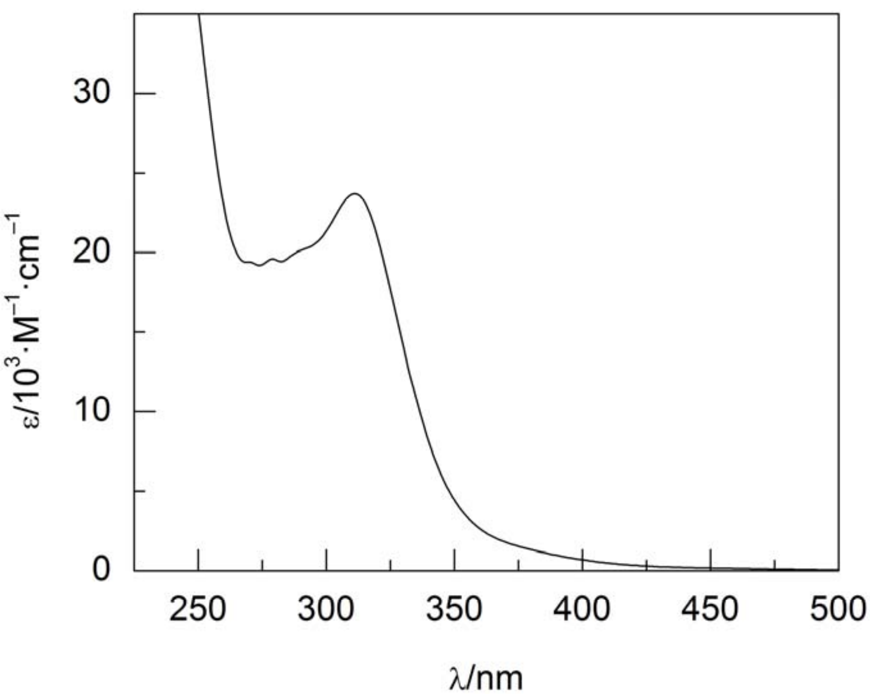

Figure S10. Electronic absorption spectrum of **4b** recorded at 293 K in THF.

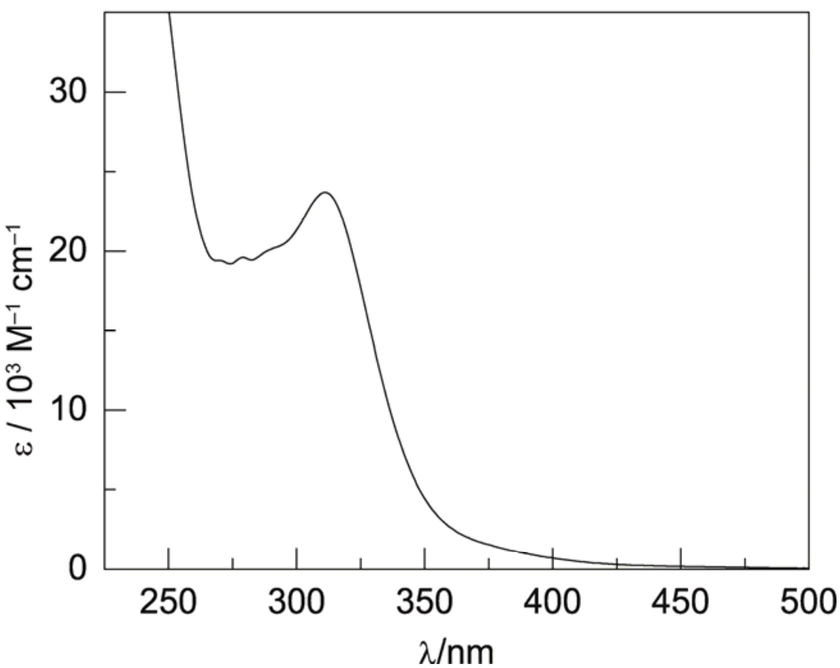

Figure S11. Electronic absorption spectrum of **4c** recorded at 293 K in THF.

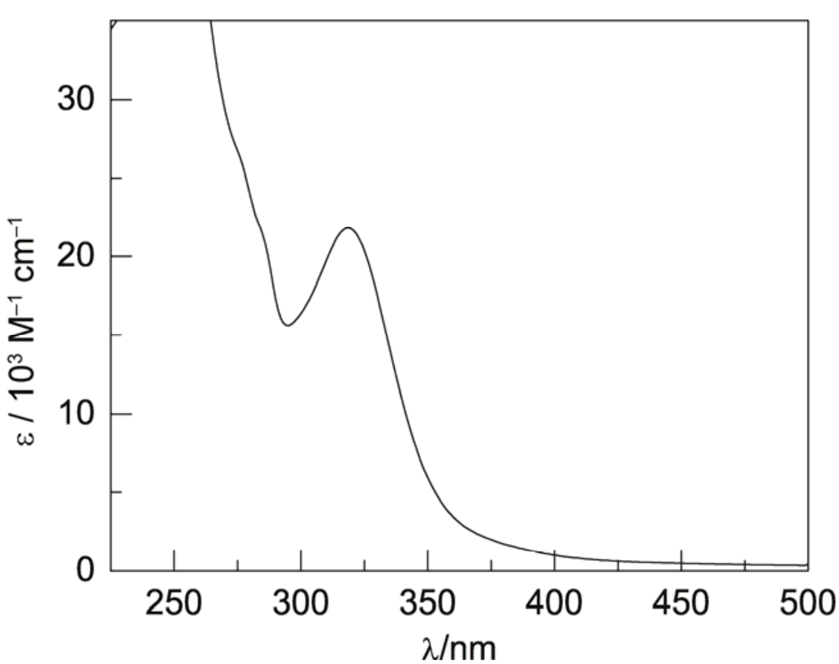

Figure S12. Electronic absorption spectrum of **4d** recorded at 293 K in THF.

Table S1. Rate constants, as defined by Eq. (6), for the reaction of **2** with HCl and O_2.

X	k_1/min^{-1} atm^{-1} M [a]	[HCl]$^{-1}$/M^{-1}	k_1^{HCl}/min^{-1} atm^{-1} [a,b]	k_1'/min^{-1} atm^{-1} [a]
F	0.0355 ± 0.0003	8.3	0.29±0.002	0.029
		11	0.39±0.003	
		17	0.60±0.005	
		33	1.17± 0.01	
Cl	0.035 ± 0.001	8.3	0.29±0.01	0.07
		11	0.39±0.01	
		17	0.60±0.02	
		33	1.16± 0.03	
Me	0.0194 ± 0.0009	8.3	0.16±0.01	0.11
		11	0.21±0.02	
		17	0.33±0.02	
		33	0.64± 0.03	
OMe	0.0160 ± 0.0004	8.3	0.13±0.003	0.03
		11	0.18±0.004	
		17	0.27±0.01	
		33	0.53± 0.01	