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## **Supporting information:**

## Density functional theory calculations of catalytic mechanistic pathways for the formation of O<sub>2</sub> involving Triazolylidene Iridium Complexes

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Step I:  $[Ir^{III}-OH_2]^+$  to  $[Ir^{1V}-OH]^+$  and Step II:  $[Ir^{IV}-OH]^+$  to  $[Ir^{V}=O]^+$ 

The reduction potentials are calculated by the standard reduction free energy in solution, i.e.,

$$nFE^o = \Delta G_{(sol)}$$

Step I:  $[Ir^{III}-OH_2^+]/[Ir^{1V}-OH^+]$ 

$$[Ir^{IV}-OH_2]^{+2} \xrightarrow{-H^+} [Ir^{IV}-OH]^{+1}$$

$$\uparrow -e^- \qquad \uparrow -e^-$$

$$[Ir^{III}-OH_2]^+ \xrightarrow{-H^+} [Ir^{III}-OH]^0$$

**Figure S1:**  $[Ir^{III}-OH_2]^+$  to  $[Ir^{1V}-OH]^+$  proton coupled electron transfer step computed thermochemistry pathways.

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Using: E^o = \Delta G_{(sol)}/nF
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To estimate  $\Delta G_{(sol)}$ , we can use Born-Haber cycles:

Born-Haber cycle for  $[Ir^{III}-OH_2]^{+1}$  \_\_-e<sup>-</sup>  $[Ir^{IV}-OH_2]^{+2}$ 

$$[\mathrm{Ir}^{\mathrm{III}} - \mathrm{OH}_{2}^{+1}]^{+\mathrm{III}} \xrightarrow{\Delta G_{(g)}} [\mathrm{Ir}^{\mathrm{IV}} - \mathrm{OH}^{+2}]^{+\mathrm{IV}}$$

$$\downarrow \Delta G_{\mathrm{solu}}(\mathrm{II}) \qquad \qquad \downarrow \Delta G_{\mathrm{solu}}(\mathrm{III})$$

$$[\mathrm{Ir}^{\mathrm{III}} - \mathrm{OH}_{2}^{+1}]^{+\mathrm{III}} \xrightarrow{-\Delta G_{(aq)}} [\mathrm{Ir}^{\mathrm{IV}} - \mathrm{OH}_{2}^{+2}]^{+\mathrm{IV}}$$

Born-Haber cycle for [Ir<sup>III</sup>-OH]  $-e^{-}$  [Ir<sup>IV</sup>-OH]<sup>+1</sup>

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$$[Ir^{V}-OH]^{+2} \xrightarrow{-H^{+}} [Ir^{V}=O]^{+1}$$

$$\uparrow -e^{-} \qquad \uparrow -e^{-}$$

$$[Ir^{IV}-OH]^{+} \xrightarrow{-H^{+}} [Ir^{IV}=O]^{0}$$

**Figure S2:**  $[Ir^{IV}-OH]^+$  to  $[Ir^V=O]^+$  proton coupled electron transfer step computed thermochemistry pathways.

## **Pka Calculations:**

We have calculated pKa values for both reaction steps which involve proton transfer. In the literature,<sup>6b</sup> the procedure to calculate the pKa values from changes in the Gibbs free energy in solution is widely reported,<sup>6b,21-23</sup> and the reader is referred thereto for additional details.

In our case, we have calculated the pKa values by using the following equation (for room-temperature estimation), using kcal/mol units for the solvation free energy:

$$pKa = \frac{\Delta G_{(sol)}}{1.365}$$

Here, we adopt a widely accepted<sup>24</sup> value for the free energy of solvation of a proton,  $\Delta G_{solv}(H^+) = -265.9$  kcal/mol. The gas-phase Gibbs free energy is a small correction, given by  $G^{o}_{(gas)}(H^+) = 3/2kT + PV - TS = -6.98$  kcal/mol.



Figure S3: Potential energy surface of conversion of cyclic structure(7b) to linear form(7a)