

Supporting information

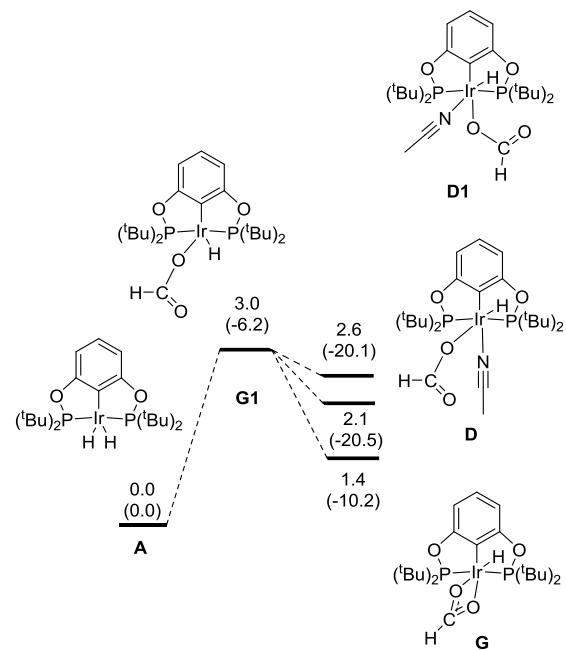
Reduced State of Iridium PCP Pincer Complexes in Electrochemical CO<sub>2</sub> Hydrogenation

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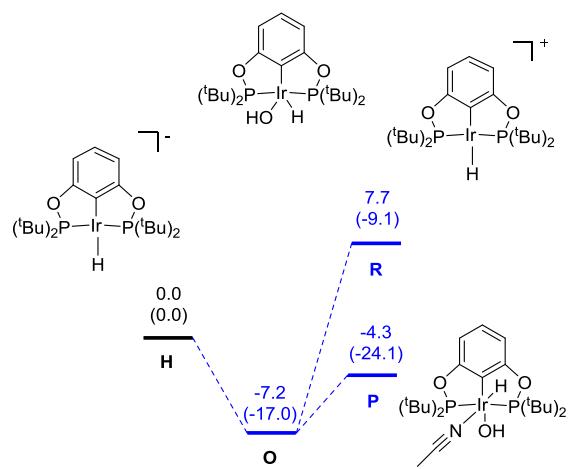
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SE-10691 Stockholm, Sweden.

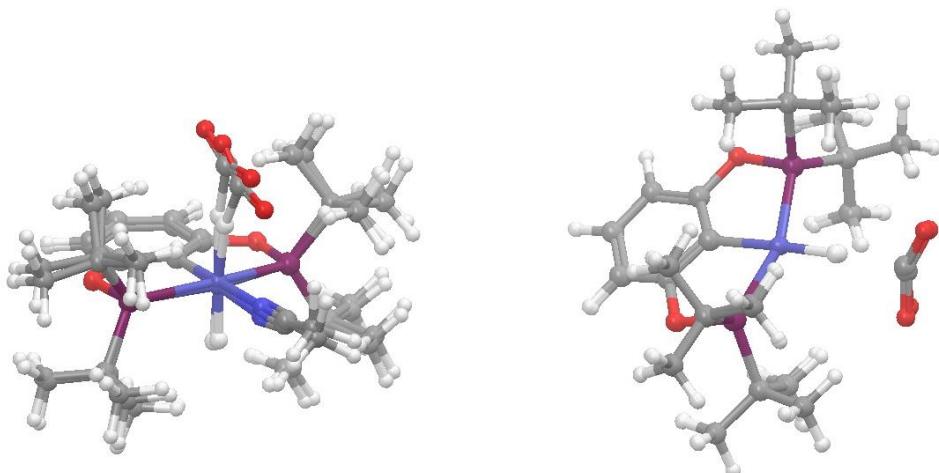
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**Scheme S1.** Gibbs free energy profile (in kcal mol<sup>-1</sup>) for complexes followed by complex **G** formation. Relative enthalpies are given in parentheses.



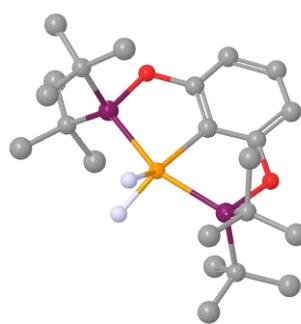
**Scheme S2.** Gibbs free energy profile (in  $\text{kcal mol}^{-1}$ ) for complexes followed by complex **O** formation. Relative enthalpies are given in parentheses.



**Figure S1.** Overlay of gas and solvent optimized transition states TS1 (left) and TS5 (right). The difference in free energy of the gas phase optimized and solvent optimized transition states is  $\sim 0.3 \text{ kcal mol}^{-1}$  for both species.

Cartesian coordinates in Å and energies in atomic units unless stated otherwise of the calculated geometries. Numbered as in article. E and G<sub>solv</sub> are given in a.u. and ZPE,  $\Delta H_{298}$  and S<sub>298</sub> in kcal/mol.

**A**



E (M06/LACV3P\*\*++ 2f(Ir)) = -1800.48046056976

ZPE (kcal mol<sup>-1</sup>) = 368.879

G<sub>water</sub> = -0.0054514

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 22.252

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 206.493

## B

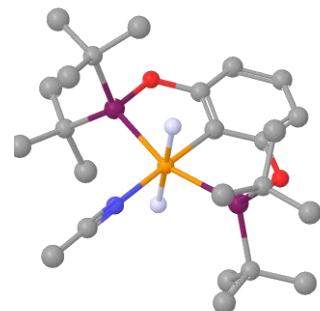
E (M06/LACV3P\*\*++ 2f(Ir)) = -1933.19042854433

ZPE (kcal mol<sup>-1</sup>) = 399.587

G<sub>water</sub> = -0.0137107

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 24.682

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 224.941



## TS 1

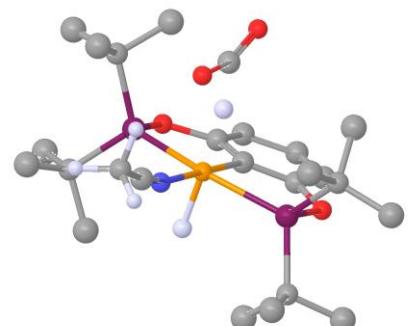
E (M06/LACV3P\*\*++ 2f(Ir)) = -2121.73876018892

ZPE (kcal mol<sup>-1</sup>) = 407.259

G<sub>water</sub> = -0.0150775

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 26.595

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 237.693



## C

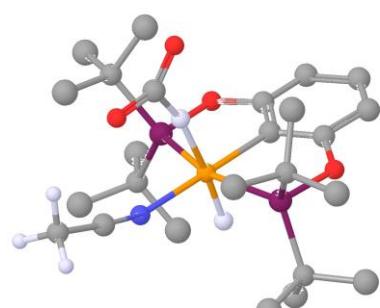
E (M06/LACV3P\*\*++ 2f(Ir)) = -2121.73953671689

ZPE (kcal mol<sup>-1</sup>) = 408.543

G<sub>water</sub> = -0.0215117

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 26.701

S<sub>298</sub> (kcal K<sup>-1</sup> mol<sup>-1</sup>)= 237.290



**D**

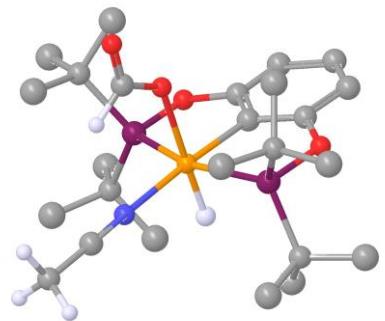
E (M06/LACV3P\*\*++ 2f(Ir)) = -2121.75127068906

ZPE (kcal mol<sup>-1</sup>) = 410.468

G<sub>water</sub> = -0.0293303

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 26.946

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 242.001

**E**

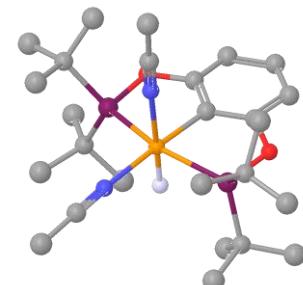
E (M06/LACV3P\*\*++ 2f(Ir)) = -2065.13996860930

ZPE (kcal mol<sup>-1</sup>) = 425.872

G<sub>water</sub> = -0.0598704

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 27.696

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 249.522

**TS2**

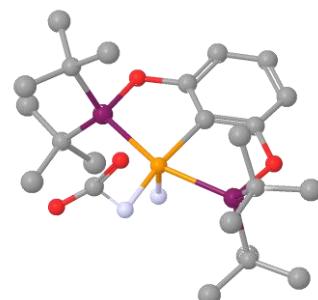
E (M06/LACV3P\*\*++ 2f(Ir)) = -1989.02216593519

ZPE (kcal mol<sup>-1</sup>) = 376.947

G<sub>water</sub> = -0.0077728

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 24.084

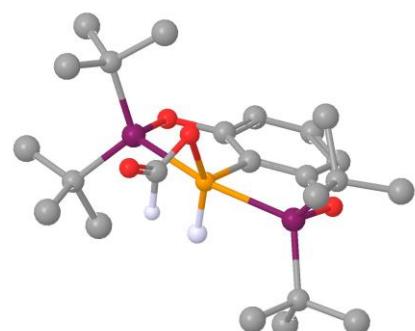
S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 220.820

**F**

E (M06/LACV3P\*\*++ 2f(Ir)) = -1989.02703239317

ZPE (kcal mol<sup>-1</sup>) = 379.199

G<sub>water</sub> = -0.0124888



$\Delta H_{298}$  (kcal mol $^{-1}$ )= 23.933

$S_{298}$  (cal K $^{-1}$  mol $^{-1}$ )= 219.530

### TS3

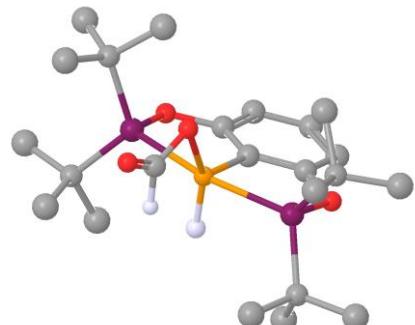
E (M06/LACV3P\*\*++ 2f[Ir]) = -1989.02380610299

ZPE (kcal mol $^{-1}$ ) = 379.254

G<sub>water</sub> = -0.0161681

$\Delta H_{298}$  (kcal mol $^{-1}$ )= 23.263

$S_{298}$  (cal K $^{-1}$  mol $^{-1}$ )= 213.529



### G

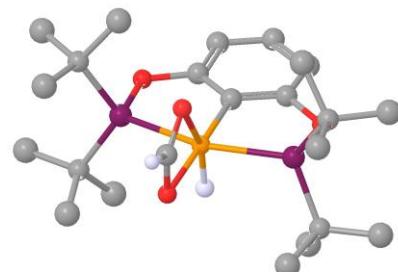
E (M06/LACV3P\*\*++ 2f[Ir]) = -1989.05576328726

ZPE (kcal mol $^{-1}$ ) = 380.786

G<sub>water</sub> = -0.0089567

$\Delta H_{298}$  (kcal mol $^{-1}$ )= 23.883

$S_{298}$  (cal K $^{-1}$  mol $^{-1}$ )= 218.737



### G1

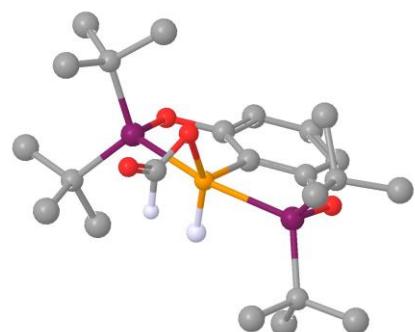
E (M06/LACV3P\*\*++ 2f[Ir]) = -1989.03649433512

ZPE (kcal mol $^{-1}$ ) = 379.042

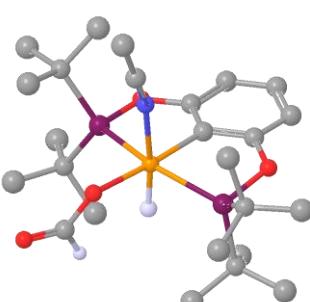
G<sub>water</sub> = -0.0202131

$\Delta H_{298}$  (kcal mol $^{-1}$ )= 24.534

$S_{298}$  (cal K $^{-1}$  mol $^{-1}$ )= 226.531



### D1



E (M06/LACV3P\*\*++ 2f(Ir)) = -2121.75003964533

ZPE (kcal mol<sup>-1</sup>) = 410.538

G<sub>water</sub> = -0.030111

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>) = 27.01

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>) 241.784

## H

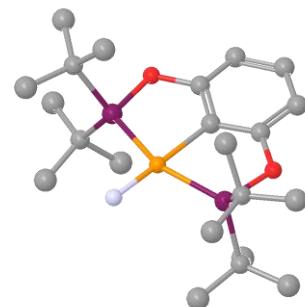
E (M06/LACV3P\*\*++ 2f(Ir)) = -1799.93267894932

ZPE (kcal mol<sup>-1</sup>) = 361.809

G<sub>water</sub> = -0.0729677

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>) = 21.959

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>) = 204.893



## TS4

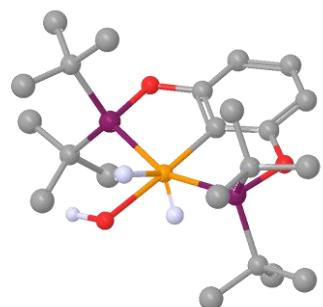
E (M06/LACV3P\*\*++ 2f(Ir)) = -1876.28842212114

ZPE (kcal mol<sup>-1</sup>) = 374.137

G<sub>water</sub> = -0.0724639

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>) = 23.092

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>) = 210.577



## TS4 + H<sub>2</sub>O

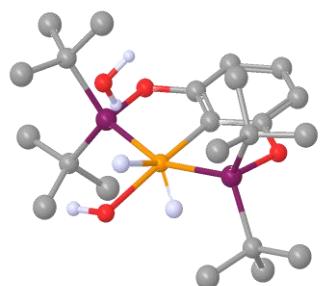
E (M06/LACV3P\*\*++ 2f(Ir)) = -1952.7193652141

ZPE (kcal mol<sup>-1</sup>) = 389.841

G<sub>water</sub> = -0.0758817

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>) = 25.076

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>) = 225.797



### **TS4+4H<sub>2</sub>O**

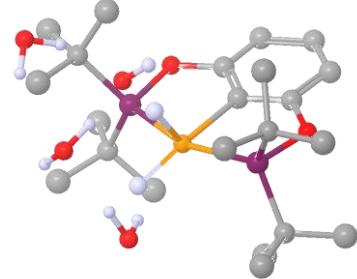
E (M06/LACV3P\*\*++ 2f(Ir)) = -2105.65937370730

ZPE (kcal mol<sup>-1</sup>) = 423.403

G<sub>water</sub> = -0.0779925

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 27.837

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 245.825



### **I**

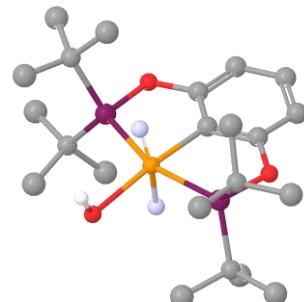
E (M06/LACV3P\*\*++ 2f(Ir)) = -1876.3525300945

ZPE (kcal mol<sup>-1</sup>) = 376.677

G<sub>water</sub> = -0.0754111

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 22.966

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 210.570



### **TS5**

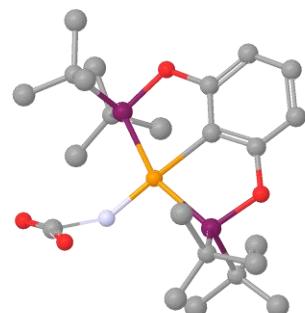
E (M06/LACV3P\*\*++ 2f(Ir)) = -1988.49663537560

ZPE (kcal mol<sup>-1</sup>) = 369.354

G<sub>water</sub> = -0.0616447

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 24.127

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 222.858

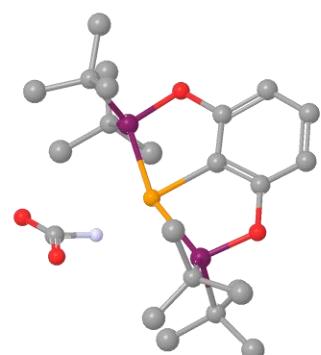


### **K**

E (M06/LACV3P\*\*++ 2f(Ir)) = -1988.50231120362

ZPE (kcal mol<sup>-1</sup>) = 371.308

G<sub>water</sub> = -0.0697106



$\Delta H_{298}$  (kcal mol $^{-1}$ )= 24.103

$S_{298}$  (cal K $^{-1}$  mol $^{-1}$ )= 223.181

## L

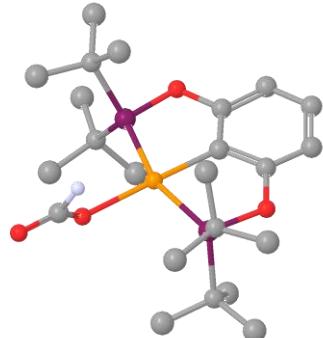
E (M06/LACV3P\*\*++ 2f[Ir]) = -1988.51812772531

ZPE (kcal mol $^{-1}$ ) = 372.391

G<sub>water</sub> = -0.0722993

$\Delta H_{298}$  (kcal mol $^{-1}$ )= 24.324

$S_{298}$  (cal K $^{-1}$  mol $^{-1}$ )= 224.493



## TS6

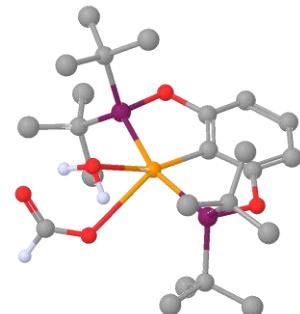
E (M06/LACV3P\*\*++ 2f[Ir]) = -2064.93492925688

ZPE (kcal mol $^{-1}$ ) = 388.918

G<sub>water</sub> = -0.0637715

$\Delta H_{298}$  (kcal mol $^{-1}$ ) = 25.157

$S_{298}$  (cal K $^{-1}$  mol $^{-1}$ ) = 226.91



## M

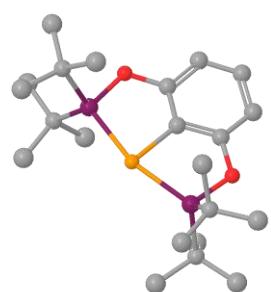
E (M06/LACV3P\*\*++ 2f[Ir]) = -1799.26344649236

ZPE (kcal mol $^{-1}$ ) = 358.89

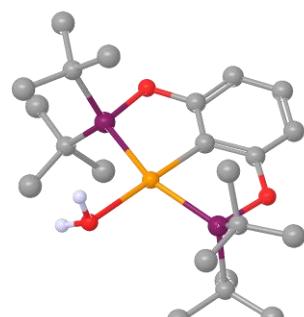
G<sub>water</sub> = -0.007875

$\Delta H_{298}$  (kcal mol $^{-1}$ )= 21.694

$S_{298}$  (cal K $^{-1}$  mol $^{-1}$ )= 203.796



## N



E (M06/LACV3P\*\*++ 2f(Ir)) = -1875.71038662996

ZPE (kcal mol<sup>-1</sup>) = 374.440

G<sub>water</sub> = -0.0176007

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 23.518

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 215.747

### TS7

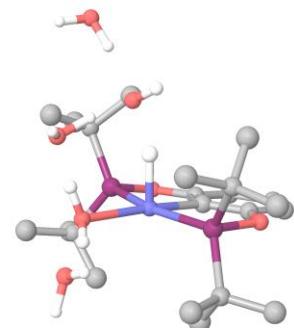
E (M06/LACV3P\*\*++ 2f(Ir)) = -1875.68106700592

ZPE (kcal mol<sup>-1</sup>) = 371.889

G<sub>water</sub> = -0.0104579

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 22.921

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 211.278



### TS7+H<sub>2</sub>O

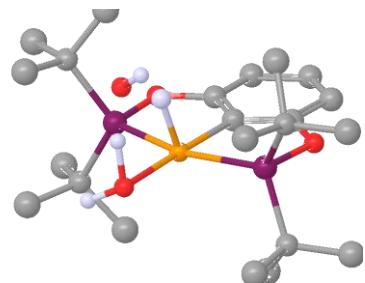
E (M06/LACV3P\*\*++ 2f(Ir)) = -1952.1208402141

ZPE (kcal mol<sup>-1</sup>) = 386.601

G<sub>water</sub> = -0.0125681

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 23.894

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 217.35



### TS7+4H<sub>2</sub>O

E (M06/LACV3P\*\*++ 2f(Ir)) = -2181.42022824913

ZPE (kcal mol<sup>-1</sup>) = 434.440

G<sub>water</sub> = -0.0378583

DH<sub>298</sub> (kcal mol<sup>-1</sup>)= 28.924

DS<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 253.034

**O**

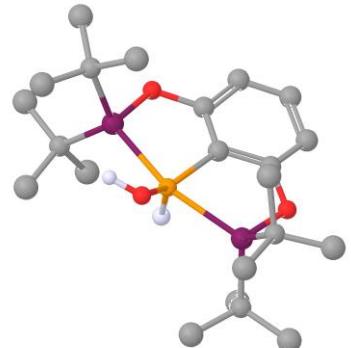
E (M06/LACV3P\*\*++ 2f(Ir)) = -1875.71679220896

ZPE (kcal mol<sup>-1</sup>) = 374.057

G<sub>water</sub> = -0.0102794

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 22.720

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 207.967

**P**

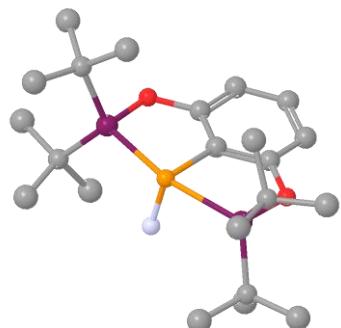
E (M06/LACV3P\*\*++ 2f(Ir)) = -1799.66170079301

ZPE (kcal mol<sup>-1</sup>) = 364.712

G<sub>water</sub> = -0.0744598

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 21.946

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 204.321

**R**

E (M06/LACV3P\*\*++ 2f(Ir)) = -2008.41418054953

ZPE (kcal mol<sup>-1</sup>) = 403.885

G<sub>water</sub> = -0.0241029

ΔH<sub>298</sub> (kcal mol<sup>-1</sup>)= 25.958

S<sub>298</sub> (cal K<sup>-1</sup> mol<sup>-1</sup>)= 234.598

