Supporting Information for

Unsaturated iridium pyridinedicarboxylate pincer complexes with catalytic activity in borylation of arenes

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Kinetic parameters for pyridine exchange in compound [Ir(κ₃-pydc)(1-κ₄,5-η-C₈H₁₃)(py)] (1-py).

The kinetic parameters for the pyridine exchange in compound 1-py were determined by NMR spectroscopy.

\[
1\text{-py} + \text{py}^* \rightarrow 1\text{-py}^* + \text{py}
\]

First-order rate constants were determined from the decay of [1-py] with time under first-order conditions using linear least-square regression analysis. Typical plots of [1-py] and [py] vs t obtained from NMR measurements using [1-py]₀ = 3.66 mM, [py*] = 0.136 M and 263.15 K are shown in Figure 1a. The ln[1-py] vs t representation provided a linear fit that is representative of a first-order kinetic transformation with the slope of the line corresponding to the observed first-order rate constant \( k \) (s⁻¹) (Figure 1b).

![Fig. 1](image)

**Fig. 1.** a) Decay of [1-py] and increase of [py] vs t at [1-py]₀ = 3.66 mM, [py*] = 0.136 M and 263.15 K. b) First-order kinetic fit of the data: ln[1-py] vs t plot.

The influence of the [py-\( d^5 \)] on the reaction rate was investigated in the concentration range 136–407 mM in CD₂Cl₂ at [1-py]₀ = 3.66 mM and 263.15 K (Figure 2).
Fig. 2. Plot of $k_{\text{obs}}$ vs [py$^*$] for pyridine exchange in 1-py.

The influence of the temperature on the reaction rate was investigated in the temperature range 248.15–268.15 K in CD$_2$Cl$_2$ at [1-py]$_0 = 3.66$ mM and [py$^*$] = 0.136 M. The rate constant was determined at five different temperatures and the overall activation parameters, $\Delta H^\#$ and $\Delta S^\#$, were determined using the logarithmic form of the Eyring equation (Figure 3).

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}$$

<table>
<thead>
<tr>
<th>T/K</th>
<th>[py$^*$]/molL$^{-1}$</th>
<th>$k_{\text{obs}}$/s$^{-1}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>268.15</td>
<td>0.1358</td>
<td>1.32 $\pm$ 0.04 E-04</td>
<td>0.985</td>
</tr>
<tr>
<td>263.15</td>
<td>0.1358</td>
<td>2.73 $\pm$ 0.01 E-05</td>
<td>0.999</td>
</tr>
<tr>
<td>258.15</td>
<td>0.1358</td>
<td>1.16 $\pm$ 0.01 E-05</td>
<td>0.998</td>
</tr>
<tr>
<td>253.15</td>
<td>0.1358</td>
<td>7.59 $\pm$ 0.04 E-06</td>
<td>0.997</td>
</tr>
<tr>
<td>248.15</td>
<td>0.1358</td>
<td>3.39 $\pm$ 0.01 E-06</td>
<td>0.999</td>
</tr>
</tbody>
</table>

$\Delta H^\# = 93 \pm 1$ kJmol$^{-1}$, $\Delta S^\# = 24 \pm 4$ JK$^{-1}$mol$^{-1}$, $\Delta G^\# = 86 \pm 2$ kJmol$^{-1}$ at 293.15 K.

Fig. 3. Eyring plot for pyridine exchange in 1-py and derived activation parameters.