Supplementary Information for

**Steric and electronic effects on acetate assisted cyclometallation of phenyl pyridines at [MCl₂Cp*]₂ (M = Ir, Rh)**

David L. Davies,*a Kuldip Singh*a and Neringa Tamosiunaitea

Department of Chemistry, University of Leicester, Leicester LE1 7RH
Figure S1 Molecular structure of ortho 2b-F 50% displacement ellipsoids and H atoms have been omitted for clarity. There is a 50:50 C1:N1 and F: H disorder. The methyl’s and ring carbon atoms of the Cp* are also disordered each over two sites (50:50).
Figure S2 Hammett plot for relative rates of formation of *meta*-cyclometallated complexes of Rh $\log(k_R/k_H)$ against $\sigma_m$.

Figure S3 Hammett plot of thermodynamic ratios $\log(K_R/K_H)$ against $\sigma_m$ for Rh.
Table S1: Deuteration of 2a,b-R in CD$_3$OD.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>M</th>
<th>Time</th>
<th>o:p</th>
<th>% D in site 5 (ortho-isomer)</th>
<th>%D in site 8 (para-isomer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CF$_3$</td>
<td>Ir</td>
<td>2 h</td>
<td>para-only$^a$</td>
<td>-</td>
<td>N.D.</td>
</tr>
<tr>
<td>2</td>
<td>CF$_3$</td>
<td>Rh</td>
<td>2 h</td>
<td>para-only$^a$</td>
<td>-</td>
<td>N.D.</td>
</tr>
<tr>
<td>3</td>
<td>OMe</td>
<td>Ir</td>
<td>2 h</td>
<td>1.1:1</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>4</td>
<td>OMe</td>
<td>Rh</td>
<td>15 min.</td>
<td>1:2.2</td>
<td>N.D.</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>OMe</td>
<td>Rh</td>
<td>2 h</td>
<td>1:2.5</td>
<td>50</td>
<td>&gt;80</td>
</tr>
</tbody>
</table>

N.D. not detected by $^1$H and $^2$H NMR spectroscopy
$^a$ No ortho-isomer was detected by $^{19}$F NMR spectroscopy

Table S2: Competition experiments to form meta-substituted complexes of Ir$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>R$_1$</th>
<th>R$_2$</th>
<th>A:B, 15 min, rt, DCM:MeOH</th>
<th>A:B, 15 min, rt, TFE</th>
<th>A:B, 2 h, 60$^\circ$C, TFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>NMe$_2$</td>
<td>1:1.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>NMe$_2$</td>
<td>-</td>
<td>1:1.2</td>
<td>1.3:1</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>Me</td>
<td>1:1.3</td>
<td>1.1:1</td>
<td>1.3:1</td>
</tr>
<tr>
<td>4</td>
<td>F</td>
<td>H</td>
<td>1:2.9</td>
<td>1:1.3</td>
<td>1.3:1$^a$</td>
</tr>
<tr>
<td>5</td>
<td>CF$_3$</td>
<td>H</td>
<td>1:5.0</td>
<td>1:1.4</td>
<td>1.7:1$^a$</td>
</tr>
<tr>
<td>6</td>
<td>CF$_3$</td>
<td>F</td>
<td>1:1.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ 90 $^\circ$C, 2 hours

Table S3: Competition experiments to form meta-substituted complexes of Rh.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R$_1$</th>
<th>R$_2$</th>
<th>DCM:MeOH</th>
<th>TFE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>A:B, 15 min., rt, 50$^\circ$C</td>
<td>A:B, 3 days, 50$^\circ$C</td>
</tr>
<tr>
<td>1</td>
<td>H</td>
<td>NMe$_2$</td>
<td>1:2.9</td>
<td>1:1.2$^a$</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>Me</td>
<td>1:1.1</td>
<td>1.2:1</td>
</tr>
<tr>
<td>3</td>
<td>F</td>
<td>H</td>
<td>1:3.8</td>
<td>1.1:1$^{b}$</td>
</tr>
<tr>
<td>4</td>
<td>CF$_3$</td>
<td>F</td>
<td>1:2.1</td>
<td>1:1.7</td>
</tr>
<tr>
<td>5</td>
<td>CF$_3$</td>
<td>H</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ 2 days; $^b$ 2 hours
Exchange of phenylpyrazole by 2-phenylpyridine

A Schlenk flask equipped was charged with the Rh phenylpyrazole complex 3b (0.0395 mmol), NaOAc (0.080 mmol) and TFE (2 mL) and 2-phenylpyridine (0.045 mmol) were added and stirred at rt. The reaction with Rh reached 80% conversion to 2b-H after 1 hour.

Scheme S1 exchange of phenylpyrazole by 2-phenylpyridine at Cp*Rh
$^1$H NMR 1a-NMe$_2$

Expansion of $^1$H NMR
$^{13}$C NMR 1a-NMe₂
$^1$H NMR 1b-NMe$_2$

Expansion of $^1$H NMR
$^{13}$C NMR 1b-NMe$_2$
\(^{1}H\) NMR 1a-Me

Expansion of \(^{1}H\) NMR of 1a-Me
$^{13}$C NMR of 1a-Me
$^1$H NMR 1b-Me

Expansion of $^1$H NMR 1b-Me
$^{13}$C NMR of 1b-Me
\textbf{\textsuperscript{1}H NMR 1a-F}

\begin{center}
\includegraphics[width=\textwidth]{1H_NMR_1a_F.png}
\end{center}

\begin{flushleft}
\textbf{Expansion of \textsuperscript{1}H NMR 1a-F}
\end{flushleft}

\begin{center}
\includegraphics[width=\textwidth]{1H_NMR_1a_F_expansion.png}
\end{center}
$^1$H NMR of 1b-F

Expansion of $^1$H NMR 1b-F
$^{19}\text{F NMR of 1b-F}$

$^{13}\text{C NMR of 1b-F}$
$^1$H NMR of 1a-CF$_3$

Expansion of $^1$H NMR of 1a-CF$_3$
$^{19}$F NMR of 1a-CF$_3$

$^{13}$C NMR of 1a-CF$_3$
$^1$H NMR of 1b-CF$_3$

Expansion of $^1$H NMR of 1b-CF$_3$
$^{19}$F NMR of 1b-CF$_3$

$^{13}$C NMR of 1b-CF$_3$
$^1$H NMR of a mixture of ortho and para 2a-OMe

Expansion of $^1$H NMR of para 2a-OMe
$^{13}$C NMR of a mixture of ortho and para 2a-OMe
$^1$H NMR of para 2b-OMe

Expansion of $^1$H NMR of para 2b-OMe
$^{13}$C NMR of para 2b-OMe
$^1$H NMR of para 2a-CF$_3$

Expansion of $^1$H NMR of para 2a-CF$_3$
$^{19}$F NMR of para 2a-CF$_3$

$^{13}$C NMR of para 2a-CF$_3$
Expansion of $^1$H NMR of para 2b-CF$_3$
$^{19}\text{F NMR of para 2b-CF}_3$

$^{13}\text{H NMR of para 2b-CF}_3$
1H NMR of a mixture of ortho and para 2a-F

Expansion of 1H NMR of a mixture of ortho and para 2a-F
$^{19}$F NMR of a mixture of ortho and para 2a-F

$^{13}$C NMR of a mixture of ortho and para 2a-F
$^1$H NMR of ortho 2b-F

Expansion of $^1$H NMR of ortho 2b-F
$^{19}F$ NMR of ortho 2b-F

$^{13}C$ NMR of ortho 2b-F