Electronic Supplementary Information

Direct transformation of 2-acetylpyridine oxime esters into α-oxygenated imines in an Ir(III) complex

Hiroyuki Takahashi, Shintaro Kodama,* and Youichi Ishii*

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

Contents

General considerations S2
Transformation of 1 into 2 S2
Synthesis of 2aBF4 S4
Synthesis of 4Cl S5
Fig. S1. ESI-MS spectrum (positive ion mode) for the reaction mixture in Scheme 3 (A crossover experiment). S6
X-ray diffraction studies S7
Table S1. X-ray crystallographic data for 2aBF4 and 4Cl. S8
Fig. S2. 1H NMR (CD2Cl2) spectrum of 2aCl. S9
Fig. S3. 1H NMR (CDCl3) spectrum of 2bCl. S10
Fig. S4. 1H NMR (CDCl3) spectrum of 2dCl. S11
Fig. S5. 1H NMR (CDCl3) spectrum of 2eCl. S12
Fig. S6. 1H NMR (CDCl3) spectrum of 2fCl. S13
Fig. S7. 1H NMR (CD2Cl2) spectrum of 2aBF4. S14
Fig. S8. 1H NMR (CDCl3) spectrum of 4Cl. S15
Fig. S9. Full 1H NMR (CD2Cl2-D2O) spectrum of 4Cl. S16
Fig. S10. Full 1H NMR (CD2Cl2-D2O-NEt3) spectrum of 4Cl-d3. S16
References S17
General considerations

All experimental manipulations for air and water sensitive reagents were carried out in dried glass vessels under an argon or a nitrogen atmosphere by standard Schlenk techniques. Dichloromethane was distilled over P₄O₁₀; methanol was distilled over Mg. They were degassed and stored under an argon atmosphere. The other solvents (anhydrous grade) were purchased from Sigma-Aldrich and purged with argon before use. ¹H (500 MHz) and ¹³C{¹H} (126 MHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer. Chemical shifts are reported in δ, referenced to residual ¹H and ¹³C signals of deuterated solvents as internal standards. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer using KBr pellets. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer.

Transformation of 1 into 2

\[
\text{R}^1 \quad \text{N} \quad \text{N} \quad \text{O} \quad \text{X} \\
\text{1a-f} \quad \xrightarrow{\text{[Cp*IrCl(\mu-Cl)]_2, CH_2Cl_2, 25 °C}} \quad \text{R}^1 \quad \text{N} \quad \text{NH} \quad \text{O} \quad \text{X} \\
\text{2a-fCl} \quad \text{Cl}
\]

General procedure

A mixture of \([\text{Cp*IrCl(\mu-Cl)]_2}\) and oxime ester 1 in dichloromethane was stirred at 25 °C for an appropriate reaction time (3–6 h). After the completion of the reaction, the mixture was filtered through a Celite pad, and the filtrate was concentrated in vacuo. The crude product was purified by recrystallization from dichloromethane–hexane or dichloromethane–methanol–diethyl ether to give 2Cl.
**Synthesis of 2aCl:** This compound was obtained from [Cp*IrCl(μ-Cl)]$_2$ (31.9 mg, 0.040 mmol) and oxime acetate 1a (14.4 mg, 0.081 mmol) according to *general procedure*. The reaction time was 3 h. The product was purified by recrystallization from dichloromethane–hexane. Dark red crystals (38.2 mg, 83% yield). $^1$H NMR (CD$_2$Cl$_2$) δ 15.7 (br s, 1H), 8.78 (d, $J = 6.0$ Hz, 1H), 8.06 (m, 2H), 7.73 (m, 1H), 5.88 (d, $J = 14$ Hz, 1H), 5.61 (d, $J = 14$ Hz, 1H), 2.13 (s, 3H), 1.89 (s, 15H); $^{13}$C$_{\{^1\text{H}\}}$ NMR (CD$_2$Cl$_2$) δ 174.4, 170.3, 155.5, 151.8, 140.1, 129.7, 127.7, 90.8, 61.9, 21.0, 9.49; IR (KBr, cm$^{-1}$) 1750 (ν$_{C=O}$), 1598 (ν$_{C=N}$), 1235 (ν$_{C-O}$); Anal. Calcd for C$_{19}$H$_{25}$Cl$_2$IrN$_2$O$_2$: C, 39.58; H, 4.37; N, 4.86. Found: C, 39.33; H, 4.45; N, 4.72.

**Synthesis of 2bCl:** This compound was obtained from [Cp*IrCl(μ-Cl)]$_2$ (59.6 mg, 0.075 mmol) and oxime acetate 1b (39.4 mg, 0.205 mmol) according to *general procedure*. The reaction time was 3 h. The product was purified by recrystallization from dichloromethane–methanol–diethyl ether. Dark red crystals (43.6 mg, 49% yield). $^1$H NMR (CDCl$_3$) δ 15.2 (br s, 1H), 8.63 (d, $J = 6.0$ Hz, 1H), 7.82 (s, 1H), 7.57 (dd, $J = 6.0$, 1.0 Hz, 1H), 5.88 (d, $J = 14$ Hz, 1H), 5.61 (d, $J = 14$ Hz, 1H), 2.63 (s, 3H), 2.12 (s, 3H), 1.90 (s, 15H); $^{13}$C$_{\{^1\text{H}\}}$ NMR (CDCl$_3$) δ 174.4, 170.1, 154.9, 152.7, 150.8, 130.3, 128.2, 90.3, 61.5, 21.7, 21.0, 9.53; IR (KBr, cm$^{-1}$) 1749 (ν$_{C-O}$), 1622 (ν$_{C-N}$), 1225 (ν$_{C-O}$); Anal. Calcd for C$_{20}$H$_{27}$Cl$_2$IrN$_2$O$_2$: C, 40.68; H, 4.61; N, 4.74. Found: C, 40.44; H, 4.59; N, 4.61.

**Synthesis of 2dCl:** This compound was obtained from [Cp*IrCl(μ-Cl)]$_2$ (15.8 mg, 0.020 mmol) and oxime carbonate 1d (9.6 mg, 0.046 mmol) according to *general procedure*. The reaction time was 3 h. The product was purified by recrystallization from dichloromethane–methanol–diethyl ether. Orange crystals (15.6 mg, 65% yield). $^1$H NMR (CDCl$_3$) δ 15.5 (br s, 1H), 8.78 (d, $J = 5.0$ Hz, 1H), 8.11 (d, $J = 7.0$ Hz, 1H), 8.06 (td, $J = 7.8$, 1.4 Hz, 1H), 7.74 (ddd, $J = 7.3$, 5.9, 1.4 Hz, 1H), 6.15 (d, $J = 14$ Hz, 1H), 5.54 (d, $J = 14$ Hz, 1H), 4.23 (q, $J = 7.0$ Hz, 2H), 1.91 (s, 15H), 1.30 (t, $J = 7.0$ Hz, 3H); $^{13}$C$_{\{^1\text{H}\}}$ NMR (CDCl$_3$) δ 173.6, 155.1, 153.9, 151.6, 140.0, 129.8, 127.7, 90.6, 65.3, 64.9, 14.3, 9.53; IR (KBr, cm$^{-1}$) 1755 (ν$_{C-O}$), 1600 (ν$_{C-N}$), 1260 (ν$_{C-O}$); Anal. Calcd for C$_{20}$H$_{27}$Cl$_2$IrN$_2$O$_3$: C, 39.60; H, 4.49; N, 4.62. Found: C, 39.23; H, 4.24; N, 4.53.
Synthesis of 2eCl: This compound was obtained from \([\text{Cp}^*\text{IrCl(\(\mu\)-Cl)}]_2\) (31.4 mg, 0.039 mmol) and oxime sulfonate 1e (18.2 mg, 0.085 mmol) according to general procedure. The reaction time was 6 h. The product was purified by recrystallization from dichloromethane–methanol–diethyl ether. Orange crystals (40.5 mg, 84% yield). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 14.4 (br s, 1H), 8.79 (d, \(J = 4.5\) Hz, 1H), 8.25 (d, \(J = 7.5\) Hz, 1H), 8.13 (td, \(J = 7.8, 1.2\) Hz, 1H), 7.79 (ddd, \(J = 7.3, 5.6, 1.6\) Hz, 1H), 5.28 (d, \(J = 13\) Hz, 1H), 5.10 (d, \(J = 13\) Hz, 1H), 2.84 (s, 3H), 1.87 (s, 15H); \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\)) \(\delta\) 174.8, 154.6, 151.6, 140.0, 129.7, 128.2, 90.6, 39.9, 39.6, 9.28; IR (KBr, cm\(^{-1}\)) 1599 (\(\nu_{C=N}\)), 1187 (\(\nu_{S=O}\)); Anal. Calcd for C\(_{18}\)H\(_{25}\)Cl\(_2\)IrN\(_2\)O\(_3\)S: C, 35.29; H, 4.11; N, 4.57 Found: C, 35.33; H, 4.01; N, 4.53.

Synthesis of 2fCl: This compound was obtained from \([\text{Cp}^*\text{IrCl(\(\mu\)-Cl)}]_2\) (62.9 mg, 0.079 mmol) and oxime sulfonate 1f (60.8 mg, 0.209 mmol) according to general procedure. The reaction time was 6 h. The product was purified by precipitation from dichloromethane–methanol–diethyl ether. Red oil (52.4 mg, 48% yield). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 14.3 (br s, 1H), 8.7 (d, \(J = 5.0\) Hz, 1H), 8.23 (d, \(J = 7.0\) Hz, 1H), 8.09 (t, \(J = 7.3\) Hz, 1H), 7.81 (d, \(J = 8.0\) Hz, 2H), 7.77 (m, 1H), 7.16 (d, \(J = 8.0\) Hz, 2H), 5.27 (d, \(J = 13\) Hz, 1H), 5.10 (d, \(J = 13\) Hz, 1H), 2.35 (s, 3H), 1.68 (s, 15H); \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\)) \(\delta\) 175.2, 154.3, 151.8, 142.5, 140.1, 140.1, 130.0, 128.9, 128.4, 126.3, 90.6, 39.8, 21.5, 9.27; IR (KBr, cm\(^{-1}\)) 1600 (\(\nu_{C=N}\)), 1184 (\(\nu_{S=O}\)); Anal. Calcd for C\(_{24}\)H\(_{29}\)Cl\(_2\)IrN\(_2\)O\(_3\): C, 41.86; H, 4.24; N, 4.07. Found: C, 41.47; H, 4.25; N, 4.14.

Synthesis of 2aBF\(_4\)
A mixture of \([\text{Cp}^*\text{IrCl}\langle\mu-\text{Cl}\rangle]_2\) (31.9 mg, 0.040 mmol) and oxime acetate 1a (15.1 mg, 0.085 mmol) in dichloromethane (7 mL) was stirred at 25 °C for 3 h. NaBF\(_4\) (11.0 mg, 0.100 mmol) was added to the resulting mixture and stirred for additional 3 h. Then, the mixture was filtered through a Celite pad, and the filtrate was concentrated in vacuo. The crude product was purified by recrystallization from dichloromethane–methanol–diethyl ether to give 2aBF\(_4\) as orange crystals (31.0 mg, 62% yield). \(^1\)H NMR (CD\(_2\)Cl\(_2\)) \(\delta\) 11.6 (br s, 1H), 8.82 (d, \(J = 5.5\) Hz, 1H), 8.16 (td, \(J = 7.6, 1.2\) Hz, 1H), 8.10 (br d, \(J = 7.5\) Hz, 1H), 7.83 (ddd, \(J = 7.3, 5.8, 1.5\) Hz, 1H), 5.53 (d, \(J = 16\) Hz, 1H), 5.44 (d, \(J = 17\) Hz, 1H), 2.25 (s, 3H), 1.82 (s, 15H); \(^{13}\)C{\(^1\)H} NMR (CD\(_2\)Cl\(_2\)) \(\delta\) 176.0, 170.1, 154.0, 152.2, 140.5, 130.8, 127.9, 90.8, 62.9, 20.8, 9.13; IR (KBr, cm\(^{-1}\)) 1751 (\(\nu\text{C=O}\)), 1600 (\(\nu\text{C=N}\)), 1234 (\(\nu\text{C–O}\)), 1084 (\(\nu\text{B–F}\)); Anal. Calcd for C\(_{19}\)H\(_{25}\)BCl\(_2\)F\(_4\)IrN\(_2\)O\(_2\): C, 36.35; H, 4.01; N, 4.46. Found: C, 36.46; H, 3.86; N, 4.44.

**Synthesis of 4Cl**

\[
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{Me}
\end{array}
\]

\[\text{3} \xrightarrow{[\text{Cp}^*\text{IrCl}\langle\mu-\text{Cl}\rangle]_2} \text{CH}_2\text{Cl}_2, 25 \, ^\circ\text{C}, 3 \, \text{h} \]

\[
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{Me}
\end{array}
\]

\[\text{4Cl} \]

A mixture of \([\text{Cp}^*\text{IrCl}\langle\mu-\text{Cl}\rangle]_2\) (47.8 mg, 0.060 mmol) and oxime ether 3 (18.9 mg, 0.126 mmol) in dichloromethane was stirred at 25 °C for 3 h. After the completion of the reaction, the mixture was concentrated in vacuo. The crude product was purified by recrystallization from dichloromethane–methanol–diethyl ether to give 4Cl as orange crystals (48.8 mg, 74% yield). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 8.84 (d, \(J = 4.5\) Hz, 1H), 8.62 (d, \(J = 8.0\) Hz, 1H), 8.27 (t, \(J = 7.5\) Hz, 1H), 7.93 (t, \(J = 6.3\) Hz, 1H), 3.95 (s, 3H), 2.98 (s, 3H), 1.80 (s, 15H); \(^{13}\)C{\(^1\)H} NMR (CDCl\(_3\)) \(\delta\) 171.6, 153.2, 151.8, 141.0, 130.5, 129.2, 90.8, 63.3, 14.5, 9.14; IR (KBr, cm\(^{-1}\)) 1610 (\(\nu\text{C=N}\)); Anal. Calcd for C\(_{18}\)H\(_{25}\)Cl\(_2\)IrN\(_2\)O: C, 39.41; H, 4.59; N, 5.11. Found: C, 39.31; H, 4.68; N, 4.83.
Fig. S1. ESI-MS spectrum (positive ion mode) for the reaction mixture in Scheme 3 (A crossover experiment).
X-ray diffraction studies

Diffraction data were collected on a Rigaku VariMax Saturn CCD diffractometer with graphite monochromated Mo-Ka radiation ($\lambda = 0.71075$ Å) at $-180$ °C. Intensity data were corrected for Lorentz and polarization effects and for an empirical absorption.$^{S1}$ All calculations were performed using the CrystalStructure$^{S2}$ crystallographic software package except for refinements, which was performed using SHELXL-97.$^{S3}$ The structures were solved by direct methods (SIR-97 for 2aBF$_4$$^{S4}$ and SIR-2011 for 4Cl$^{S5}$) and expanded using Fourier techniques. Non-hydrogen atoms were refined on $F^2$ anisotropically by full-matrix least-squares techniques. Hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Details of the X-ray diffraction study are summarized in Table S1.
Table S1. X-ray crystallographic data for 2aBF₄ and 4Cl.

<table>
<thead>
<tr>
<th></th>
<th>2aBF₄</th>
<th>4Cl·CH₃OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC</td>
<td>1555548</td>
<td>1555549</td>
</tr>
<tr>
<td>empirical formula</td>
<td>C₁₉H₂₅BCIF₄IrN₂O₂</td>
<td>C₁₉H₂₉Cl₂IrN₂O₂</td>
</tr>
<tr>
<td>formula weight</td>
<td>627.90</td>
<td>580.58</td>
</tr>
<tr>
<td>dimension of crystals</td>
<td>0.23×0.08×0.07</td>
<td>0.18×0.171×0.089</td>
</tr>
<tr>
<td>crystal system</td>
<td>orthorhombic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P2₁2₁2₁ (#19)</td>
<td>P2₁/c (#14)</td>
</tr>
<tr>
<td>a [Å]</td>
<td>7.5430(10)</td>
<td>11.7603(11)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>12.7445(17)</td>
<td>12.1239(12)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>22.732(3)</td>
<td>15.2286(15)</td>
</tr>
<tr>
<td>α [°]</td>
<td>90.0000</td>
<td>90.0000</td>
</tr>
<tr>
<td>β [°]</td>
<td>90.0000</td>
<td>91.3973(15)</td>
</tr>
<tr>
<td>γ [°]</td>
<td>90.0000</td>
<td>90.0000</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>2185.2(6)</td>
<td>2170.7(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;calc&lt;/sub&gt; [g cm&lt;sup&gt;−3&lt;/sup&gt;]</td>
<td>1.908</td>
<td>1.776</td>
</tr>
<tr>
<td>F(000)</td>
<td>1216</td>
<td>1136</td>
</tr>
<tr>
<td>μ [cm&lt;sup&gt;−1&lt;/sup&gt;]</td>
<td>63.005</td>
<td>64.289</td>
</tr>
<tr>
<td>trans. factors range</td>
<td>0.444–0.643</td>
<td>0.362–0.564</td>
</tr>
<tr>
<td>index ranges</td>
<td>–9 ≤ h ≤ 9</td>
<td>–15 ≤ h ≤ 13</td>
</tr>
<tr>
<td></td>
<td>–16 ≤ k ≤ 12</td>
<td>–15 ≤ k ≤ 15</td>
</tr>
<tr>
<td></td>
<td>–29 ≤ l ≤ 29</td>
<td>–19 ≤ l ≤ 19</td>
</tr>
<tr>
<td>no. rflns measured</td>
<td>17827</td>
<td>17299</td>
</tr>
<tr>
<td>no. unique rflns</td>
<td>8521</td>
<td>8138</td>
</tr>
<tr>
<td>R&lt;sub&gt;int&lt;/sub&gt;</td>
<td>0.0385</td>
<td>0.0330</td>
</tr>
<tr>
<td>no. rflns (I &gt; 2σ(I))</td>
<td>5000</td>
<td>4889</td>
</tr>
<tr>
<td>no. params refined</td>
<td>271</td>
<td>347</td>
</tr>
<tr>
<td>R₁ (I &gt; 2σ(I))&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.0269</td>
<td>0.0253</td>
</tr>
<tr>
<td>R (All cata)</td>
<td>0.0315</td>
<td>0.0296</td>
</tr>
<tr>
<td>wR&lt;sup&gt;2&lt;/sup&gt; (All cata)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.0545</td>
<td>0.0622</td>
</tr>
<tr>
<td>GOF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.994</td>
<td>1.098</td>
</tr>
<tr>
<td>max diff peak/hole [e Å&lt;sup&gt;−3&lt;/sup&gt;]</td>
<td>1.70/−2.09</td>
<td>0.76/−2.15</td>
</tr>
</tbody>
</table>

<sup>a</sup> R₁ = Σ||F<sub>o</sub>|| − |F<sub>c</sub>|| / Σ|F<sub>o</sub>|.  
<sup>b</sup> wR<sup>2</sup> = [Σ{w(F<sub>o</sub>² − F<sub>c</sub>²)²} / Σw(F<sub>o</sub>²)²]¹/², w = 1 / [σ²F<sub>o</sub>² + (aP)² + bP]  
(a and b are constants suggested by the refinement program; P = [max(F<sub>o</sub>²,0) + 2F<sub>c</sub>²] / 3).  
<sup>c</sup>GOF = [Σw(F<sub>o</sub>² − F<sub>c</sub>²)² / (N<sub>obs</sub>−N<sub>params</sub>)]¹/².
Fig. S2. $^1$H NMR (CD$_2$Cl$_2$) spectrum of 2aCl.
Fig. S3. $^1$H NMR (CDCl$_3$) spectrum of 2bCl.
Fig. S4. ¹H NMR (CDCl₃) spectrum of 2dCl.
Fig. S5. 1H NMR (CDCl₃) spectrum of 2eCl.
Fig. S6. $^1$H NMR (CDCl$_3$) spectrum of 2Cl.
Fig. S7. $^1$H NMR (CD$_2$Cl$_2$) spectrum of 2aBF$_4$. 
Fig. S8. $^1$H NMR (CDCl₃) spectrum of 4Cl.
Fig. S9. Full $^1$H NMR (CD$_2$Cl$_2$-D$_2$O) spectrum of 4Cl.

Fig. S10. Full $^1$H NMR (CD$_2$Cl$_2$-D$_2$O-NEt$_3$) spectrum of 4Cl-$d_3$. 
References


