General procedure for the hydrogenation of Ir(PHOX) complexes at the NMR scale:
In a glove-box, the iridium complex was weighed into an NMR tube, which was then filled with deuterated solvent under an argon atmosphere and put in a long narrow Schlenk tube sealed with a rubber septum. The sample was then thermostated at the desired temperature. A cooling mantle filled with dry-ice was placed around the upper part of the Schlenk in order to avoid evaporation of the deuterated solvent. Hydrogen gas (quality >99.99%) was introduced through a long stainless-steel needle. The needle was attached to a three-way stop-cock allowing to purge the whole apparatus by three argon-vacuum cycles before switching to hydrogen. The gas was bubbled through the solution at flow rates between 2 to 5 mL/min. The NMR tube was finally sealed with a rubber septum and introduced into the NMR spectrometer (Bruker Avance 500) pre-cooled to the desired temperature.

Representative $^1$H and $^{31}$P NMR data for complexes C-1, C-2 and D-2:

<table>
<thead>
<tr>
<th>hydrido-Ir complex</th>
<th>$^1$H $\delta$ (ppm)</th>
<th>$^{31}$P$^1$H $\delta$ (ppm)</th>
<th>$^2$$J$(H,H)</th>
<th>$^2$$J$(H,P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>-12.7</td>
<td>-15.6</td>
<td>4.9</td>
<td>6.8 Hz</td>
</tr>
<tr>
<td>C-2</td>
<td>-17.3</td>
<td>-29.5</td>
<td>6.8</td>
<td>7.0 Hz</td>
</tr>
<tr>
<td>D-2</td>
<td>-17.6</td>
<td>-29.8</td>
<td>7.4</td>
<td>7.0 Hz</td>
</tr>
</tbody>
</table>
$^1$H Spectrum of [(PHOX)Ir(COD)]BAr$_F$ [(PHOX)Ir(H)$_2$(COD)]BAr$_F$ C-1

(500 MHz; [D8]-THF) at -40°C
$^{31}$P-$^1$H Spectrum of [(PHOX)Ir(H)₂(COD)]BAr$_5$ C-1 (500 MHz; [D₈]-THF) at -40°C
**$^1$H and $^{31}$P{$^1$H} NMR data of [(PHOX)Ir(H)$_2$(COD)]BAr$_F$ C-1**

(500 MHz; [D8]-THF) at -40°C

**$^1$H NMR (500 MHz, [D8]-THF):** $\delta$ (ppm) 8.45 (m, 2H, H$_{Ar}$), 8.20-7.35 (m, 12H, H$_{Ar}$) among which: 7.82 (1H, H$_{Ar}$ ortho = H6), 7.52 (1H, H$_{Ar}$ ortho = H5), 5.78 (bs, 1H, CH$_{ol}$COD = H4), 5.51 (bs, 1H, CH$_{ol}$COD), 5.25 (bs, 1H, CH$_{ol}$COD), 5.10-4.90 (m, 1H, H$_{oxa}$), 4.80-4.70 (m, 2H, H$_{oxa}$), 4.72 (bs, 1H, CH$_{ol}$COD = H8), 3.93 (m, 1H, CH$_2$COD), 2.81 (m, 1H, CH$_2$COD), 2.68 (m, 1H, CH$_2$COD = H7), 2.63 (m, 1H, CH$_2$COD), 2.60 (m, 1H, CH$_2$COD), 2.30 (m, 1H, CH$_2$COD), 2.29 (m, 1H, CH$_2$COD), 1.95 (m, 1H, CH$_2$COD), 2.22 (m, 1H, CH$_{iPr}$ = H3), 1.00 (d, 3H, CH$_3$ iPr), -0.15 (d, 3H, CH$_3$ iPr), -12.7 (dd, 1H, H$_{hydride}$ = H1), -15.6 (dd, 1H, H$_{hydride}$ = H2).

**$^{31}$P{$^1$H} NMR (202.5 MHz, [D8]-THF):** $\delta$ (ppm) 4.9.

*) Identification of protons H5 and H6 (in ortho position on the two phenyl substituents of the P-atom) is based on a $^1$H {$^{31}$P} NMR spectra.

*) A NOE map of the representative interactions between hydrides and the ligand backbone as well as a three-dimensional representation of isomer C-I are depicted on the next page.
\(^1\)H and \(^{31}\)P\(^{1}\)H\} NMR data of [(PHOX)Ir(H)\(_2\)(solvent)\(_2\)]BAr\(_E\) (C-2 & D-2)

(500 MHz; [D8]-THF) at 0°C

**C-2:** \(^1\)H NMR (500 MHz, [D8]-THF): \(\delta\) (ppm) 8.35 (m, 2H \(_{\text{Ar}}\)), 7.80-6.90 (m, 12H, \(_{\text{Ar}}\)), 4.79-4.43 (m, 3H, \(_{\text{oxa}}\)), 2.33 (m, 1H, CH\(_{iPr}\)), 0.90 (d, 3H, CH\(_3\)\(_{iPr}\)), 0.35 (d, 3H, CH\(_3\)\(_{iPr}\)), -17.3 (dd, 1H, H\(_{\text{hydride}}\)), -29.5 (dd, 1H, H\(_{\text{hydride}}\));

\(^{31}\)P\(^{1}\)H\} NMR (202.5 MHz, [D8]-THF): \(\delta\) (ppm) 6.8.

**D-2:** \(^1\)H NMR (500 MHz, [D8]-THF): \(\delta\) (ppm) 8.15 (m, 2H \(_{\text{Ar}}\)), 7.80-6.90 (m, 12H, \(_{\text{Ar}}\)), 4.79-4.3 (m, 3H, \(_{\text{oxa}}\)), 3.81 (bd, 1H, CH\(_{ol\,COD}\)), 2.18 ? (m, 1H, CH\(_{iPr}\)), 0.89 (d, 3H, CH\(_3\)\(_{iPr}\)), 0.39 (d, 3H, CH\(_3\)\(_{iPr}\)), -17.6 (dd, 1H, H\(_{\text{hydride}}\)), -29.8 (dd, 1H, H\(_{\text{hydride}}\));

\(^{31}\)P\(^{1}\)H\} NMR (202.5 MHz, [D8]-THF): \(\delta\) (ppm) 7.4.
$^1$H spectra of [(PHOX)Ir(H)$_2$(solvent)$_2$]BAr$_6$ (C-2 & D-2)

(500 MHz; [D8]-THF) at 0°C (δ from -1 to 5.5 ppm)
$^1$H spectra of [(PHOX)Ir(H)$_2$(solvent)$_2$]BAr$_5$ (C-2 & D-2)

(500 MHz; [D8]-THF) at 0°C (δ from -1 to 5.5 ppm)
*) Discrimination between isomer C-2 and D-2 is based on the observed NOE contact between the apical hydride ($\delta = -29.5$ ppm) and the proton of the iso-propyl substituent ($\delta = 2.33$ ppm) of the oxazoline ring.
$^{31}$P/$^{1}$H spectra of [(PHOX)Ir(H)$_2$(solvent)$_2$]BAr$_F$ (C-2 & D-2)

(500 MHz; [D8]-THF) at 0°C
Representative bond lengths and angle for calculated isomers A2-D2

<table>
<thead>
<tr>
<th>solvato-complex</th>
<th>Rel. E (kcal/mol)</th>
<th>Ir-P (Å)</th>
<th>Ir-N (Å)</th>
<th>N-Ir-P (°)</th>
<th>Ir-H(1) (Å)</th>
<th>Ir-H(2) (Å)</th>
<th>Ir-S(1) (Å)</th>
<th>Ir-S(2) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-2</td>
<td>-</td>
<td>2.24</td>
<td>2.22</td>
<td>87.54</td>
<td>1.55</td>
<td>1.59</td>
<td>2.60</td>
<td>2.73</td>
</tr>
<tr>
<td>D-2</td>
<td>+5.0</td>
<td>2.23</td>
<td>2.20</td>
<td>88.86</td>
<td>1.54</td>
<td>1.59</td>
<td>2.57</td>
<td>5.96</td>
</tr>
<tr>
<td>A-2</td>
<td>+ 8.6</td>
<td>2.42</td>
<td>2.03</td>
<td>87.47</td>
<td>1.55</td>
<td>1.62</td>
<td>2.47</td>
<td>2.73</td>
</tr>
<tr>
<td>B-2</td>
<td>+ 14.7</td>
<td>2.42</td>
<td>2.04</td>
<td>88.2</td>
<td>1.55</td>
<td>1.62</td>
<td>2.47</td>
<td>2.76</td>
</tr>
</tbody>
</table>

S = ClCH3; Ir-(S) = Ir-Cl distance