SUPLEMENTARY MATERIAL

for

“On-Water” Rhodium-Catalysed Hydroformylation for the Production of Linear Alcohols.

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Experimental details

General:
Gas chromatography (GC) analyses were performed on a Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector (FID) on an Ultra-2 column (HP?) (25 m, 200 μm, film thickness: 0.33 μm).

Method:
80ºC to 280ºC with a slope of 10ºC min⁻¹, then holding the temperature at 280ºC for 2 min.

1-octene (Aldrich) was distilled before use. Ethanol and isopropanol were dried on molecular sieves and degassed before use. Rhodium sources were purchased from commercial sources, stored under argon and used as received.

General procedure for nonanal hydrogenation:
Reactions were performed in home-made 10 mL autoclaves equipped with a magnetic stirrer bar. The autoclave was charged with [Rh(CO)₂(acac)] (10 μmol; cod = 1,5-cyclooctadiene), alkene (2 mmol, S/Rh=200) and ligand (30 μmol, L/Rh= 3 for Xantphos; 40 μmol, L/Rh = 4 for PBU₅) and the desired solvent under argon atmosphere. The autoclave was purged three times with H₂ (P=10 bar) to remove the remaining argon from the autoclave. Subsequently, the autoclave was pressurised with CO and H₂ to the desired pressure and heated to reaction temperature using an oil bath. After a certain reaction time, the autoclave was cooled to room temperature. One drop of the reaction mixture was extracted with ether, the organic phase poured into a GC vial, diluted with dichloromethane and analysed by GC.

General procedure for 1-octene hydroformylation-hydrogenation:
The reaction profiles were obtained using a home-made magnetically stirred 75 mL autoclave equipped with a high pressure sampling system. The solids were introduced first into the autoclave, previously purged with argon, after which the liquids were added (solvent, 1-octene, P⁸Bu₅). The autoclave was then purged three times with H₂ (P=10 bar) to remove the remaining argon. Subsequently, the autoclave was pressurised with CO and H₂ to the desired pressure and heated to reaction temperature. Samples were taken out regularly and analysed by GC.

When using Xantphos as ligand, the solvent (water-isopropanol mixtures) did not need to be degassed, the reaction giving similar results with non-degassed solvents.
Calibration curves. Internal standard is n-dodecane
Nonanal reduction using PBu$_3$ as ligand

\[
\text{2 mmol} \quad \text{[Rh(CO)$_2$(acac)] S/Rh=200} \quad \text{PBu}_3 \quad \text{P/Rh=4} \quad \text{CO / H$_2$ 36 bar 1/2} \quad 80^\circ\text{C, 60 min.} \quad \text{2 mmol OH}
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>conversion</th>
<th>alcohol selectivity (%)</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>MeOH</td>
<td>61.7</td>
<td>5.7$^a$</td>
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<tr>
<td>2</td>
<td>H$_2$O/MeOH 1/1</td>
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<td>&gt;98</td>
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<td>4</td>
<td>H$_2$O/MeOH 9/1</td>
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<td>&gt;98</td>
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</table>

$^a$ 36.1% of 1,1'-dimethoxynonane was formed.

Nonanal reduction using PPh$_3$ as ligand

\[
\text{2 mmol} \quad \text{Rh(CO)$_2$(acac) S/Rh=200} \quad \text{PPh}_3 \quad \text{CO / H$_2$ 1/2 36 bar} \quad 60 \text{ min}
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>P/Rh ratio</th>
<th>T</th>
<th>conversion</th>
<th>alcohol selectivity (%)$^b$</th>
<th>catalyst decomposition$^a$</th>
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</thead>
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<td>110</td>
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<td>31.4</td>
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<td>13.6</td>
<td>57.3</td>
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<td>20.0</td>
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</tr>
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<td>13</td>
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<td>110</td>
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<td>55.4</td>
<td>Yes</td>
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<td>14</td>
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<td>110</td>
<td>13.5</td>
<td>71.8</td>
<td>No</td>
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<td>15</td>
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<td>50</td>
<td>110</td>
<td>11.6</td>
<td>64.9</td>
<td>No</td>
</tr>
</tbody>
</table>

$^a$ acetals are present as traces and mainly aldol condensation products are formed. $^b$ black colloidal solution obtained at the end of the reaction.
Nonanal reduction using Ru$_3$(CO)$_{12}$ / Xantphos

![Chemical structure](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>T (°C)</th>
<th>P (CO/H$_2$)</th>
<th>solvent</th>
<th>Alcohol yield</th>
<th>Acetal yield</th>
</tr>
</thead>
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<tr>
<td>1</td>
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<td>20 (0/20)</td>
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<tr>
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<td>36 (12/24)</td>
<td>iPrOH</td>
<td>0.4</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>3</td>
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<td>36 (12/24)</td>
<td>iPrOH</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>4</td>
<td>160</td>
<td>36 (12/24)</td>
<td>iPrOH</td>
<td>1.8</td>
<td>3.5</td>
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<tr>
<td>5</td>
<td>160</td>
<td>36 (12/24)</td>
<td>iPrOH/H$_2$O (9/1)</td>
<td>5.4</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>160</td>
<td>36 (12/24)</td>
<td>iPrOH/H$_2$O (1/1)</td>
<td>6.9</td>
<td>0.9</td>
</tr>
<tr>
<td>7</td>
<td>160</td>
<td>36 (12/24)</td>
<td>iPrOH/H$_2$O (1/9)</td>
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<td>0.4</td>
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<td>160</td>
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<td>MeOH/H$_2$O (1/9)</td>
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<td>160</td>
<td>36 (12/24)</td>
<td>toluene/H$_2$O (1/9)</td>
<td>23</td>
<td>/</td>
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<tr>
<td>10</td>
<td>160</td>
<td>36 (12/24)</td>
<td>EtOH/H$_2$O (1/9)</td>
<td>46.4</td>
<td>0</td>
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<tr>
<td>11</td>
<td>160</td>
<td>36 (12/24)</td>
<td>tAmOH/H$_2$O (1/9)</td>
<td>29.2</td>
<td>0</td>
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<tr>
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<td>160</td>
<td>36 (12/24)</td>
<td>THF/H$_2$O (1/9)</td>
<td>28.4</td>
<td>/</td>
</tr>
<tr>
<td>13</td>
<td>160</td>
<td>36 (12/24)</td>
<td>H$_2$O</td>
<td>29.8</td>
<td>/</td>
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</table>
Reaction profile of reaction Table 2, entry 1, Table 3, entry 1.

Rh(CO)$_2$(acac) 0.1 mol%
Xantphos 0.3 mol%
iPrOH / H$_2$O (1/9)
CO/H$_2$ (36 bar 1/2)
160°C, 6h

[Diagrams showing the reaction profile over time]
Reaction profile of reaction Table 2, entry 2.

Rh(CO)$_2$(acac) 0.1 mol%
Xantphos 0.3 mol%
iPrOH / H$_2$O (1/9)
CO/H$_2$ (36 bar 1/2)
100°C, 3h
then
160°C, 6h

1-octene
internal octenes
octane
aldehyde
alcohol

alcohol selectivity
l/b alcohol
Gas chromatograms of reaction Table 2, entry 3.

Rh(CO)$_2$(acac) 0.1 mol%
Xanthos 0.3 mol%
iPrOH / H$_2$O (1/9)
CO/H$_2$ (36 bar 1/2)
110ºC, 4h
then
160ºC, 20h

**Chromatogram after 4h at 110ºC**

**Chromatogram after 24h (110ºC for 4h, then 20h at 160ºC)**

93.2% linear alcohol
Reaction profile of reaction Table 3, entries 3 and 4.

\[
\text{Rh(CO)\textsubscript{2}(acac) 0.1 mol\%} \xrightarrow{\text{PBU\textsubscript{3} 0.4 mol\%}} \text{MeOH:H\textsubscript{2}O 1:3} \xrightarrow{\text{CO:H\textsubscript{2} 1:2 36 bar}} \text{(5) OH}
\]

10 mmol
1.0 M

80°C

1-octene
isomerisation
octane
aldehyde
alcohol

alcohol selectivity
l/b alcohol

S9
Reaction profile of reaction Table 3, entry 5 (1-decene used as substrate).

Rh(CO)$_2$(acac) 0.1 mol\%
Xantphos 0.3 mol\%
iPrOH / H$_2$O (1/9)
CO/H$_2$ (36 bar 1/2)
110$^\circ$C, 4h
then
160$^\circ$C, 20h
Reaction profile of reaction Table 3, entry 6 (1-dodecene used as substrate).

\[ \text{Rh(CO)}_2(\text{acac}) \ 0.1 \ \text{mol}\% \]

\[ \text{Xantphos} \ 0.3 \ \text{mol}\% \]

\[ \text{iPrOH} / \text{H}_2\text{O} (1/9) \]

\[ \text{CO/H}_2 \ (36 \ \text{bar} \ 1/2) \]

\[ 110^\circ\text{C}, \ 4\text{h} \]

then

\[ 160^\circ\text{C}, \ 20\text{h} \]

![Graph showing reaction profile with 1-dodecene, isomerisation, aldehyde, alcohol, and dodecane]
Reaction profile of reaction Table 3, entry 7 (2-octene used as substrate).

**Chemical Reaction:***

\[ \text{Rh(CO)}_2(\text{acac}) \ 0.1 \ \text{mol}\% \]
\[ \text{Xantphos} \ 0.3 \ \text{mol}\% \]
\[ \text{iPrOH} / \text{H}_2\text{O} (1/9) \]
\[ \text{CO/H}_2 \ (36 \ \text{bar} 1/2) \]
\[ 160^\circ \text{C}, 6\text{h} \]

**Graph:***

- **Aldehyde**
- **Alcohol**
- **Octenes**
- **Octane**

**Time (min):** 0 to 400

**Concentrations:**

- 10 mmol 1.0 M

**Additional Data:**

- 1-nonanol
- 2-methylpentan-1-ol
- 3-ethylheptan-1-ol
- 4-propylhexan-1-ol

**Time (min):** 0 to 2000

**Concentrations:**

- 0 to 35
Reaction profile of reaction Table 3, entries 8-9 (2-octene used as substrate).

Rh(CO)$_2$(acac) 0.1 mol%  
PBU$_3$ 0.4 mol%  
MeOH:H$_2$O 1:3  
CO:H$_2$ 1:2 36 bar  
80°C
Reaction profile of reaction Table 3, entries 10-11 (*cis*-cyclooctene used as substrate).

\[ \text{Rh(CO)}_2(\text{acac}) \; 0.1 \text{ mol}\% \]
\[ \text{PBu}_3 \; 0.4 \text{ mol}\% \]
\[ \text{MeOH:}\text{H}_2\text{O} \; 1:3 \]
\[ \text{CO:}\text{H}_2 \; 1:2 \; 36 \text{ bar} \]
\[ 80^\circ\text{C} \]
Parameter screening for cobalt-catalyzed hydroformylation of 1-octene

Table S7. Pressure and temperature optimization using Co$_2$(CO)$_8$ as catalyst.

<table>
<thead>
<tr>
<th>entry</th>
<th>T°C</th>
<th>P(H$_2$) (bar)</th>
<th>P(CO) (bar)</th>
<th>Conv. octane</th>
<th>aldehyde/alcohol</th>
<th>l/b ratio*</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>170</td>
<td>50</td>
<td>25</td>
<td>100</td>
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<td>0.9</td>
</tr>
<tr>
<td>2</td>
<td>170</td>
<td>24</td>
<td>12</td>
<td>100</td>
<td>6.8</td>
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<td>130</td>
<td>24</td>
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<td>93.8</td>
<td>9.9</td>
<td>18.6</td>
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<td>110</td>
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<td>65.7</td>
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<td>18</td>
<td>87.4</td>
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* ratio linear branched for combined aldehydes and alcohols products

Table S8. Various ligands at 110°C.

<table>
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<th>entry</th>
<th>L (L/Co ratio)</th>
<th>Conv. octane</th>
<th>aldehyde/alcohol</th>
<th>l/b ratio*</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>89.5</td>
<td>9.5</td>
<td>65.7</td>
</tr>
<tr>
<td>2</td>
<td>2,6-Ph$_2$-pyridine (4)</td>
<td>91.1</td>
<td>8.7</td>
<td>&gt;100</td>
</tr>
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<td>P$^t$Bu$_3$ (1)</td>
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<td>0</td>
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</tr>
<tr>
<td>4</td>
<td>IPr (1)</td>
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<td>n.d.</td>
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<td>NBD (10)</td>
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<td>PBr$_3$ (1)</td>
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* ratio linear branched for combined aldehydes and alcohols products
Table S9. Various ligands at 110°C and 150°C.

<table>
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<th>aldehyde/alcohol</th>
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<td>2</td>
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<td>n.d.</td>
<td>n.d.</td>
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<td>100</td>
<td>6.3</td>
<td>3.0</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
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<td>7.5</td>
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<tr>
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<td>22</td>
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<td>&gt;100</td>
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<td>PPh₂(2-OMe-C₆H₄) (2)</td>
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<td>12.9</td>
<td>1.7</td>
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<td>P(O-2,4-′Bu₂-C₆H₃)₃ (2)</td>
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<td>7.7</td>
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<td>PCy₃ (2)</td>
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* ratio linear branched for combined aldehydes and alcohols products