Supporting Information for

Tandem Ammonia Borane Dehydrogenation/Alkene Hydrogenation Mediated by [Pd(NHC)(PR$_3$)] (NHC= N-heterocyclic carbene) Catalysts

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# Contents

1. General considerations ........................................................................................................ S3
2. Dehydrogenation experiments.............................................................................................. S3
3. Kinetic experiments ............................................................................................................... S4
4. Optimization of reaction conditions.[a] .................................................................................. S5
5. Hydrogenation .................................................................................................................... S5
   5.1 Typical procedure for the hydrogenation of alkenes ........................................................ S5
   1,2-diphenylethane (Table 2, entry 1)[1] ................................................................................... S6
   1,2-diphenylpropane (Table 2, entry 2) ................................................................................... S6
   1,1-diphenylethane (Table 2, entry 3) .................................................................................... S6
   4-propylanisole (Table 2, entry 4)[2] ....................................................................................... S6
   1-propylbenzene, (Table 2, entry 5)[3] .................................................................................... S6
   methyl-3-phenylpropionate, (Table 2, entry 6) ...................................................................... S7
   1,3-diphenylpropan-1-ol, (Table 2, entry 7)[4] ..................................................................... S7
   cyclohexanol, (Table 2, entry 8)[5] ....................................................................................... S7
   cyclooctene, (Table 2, entry 9) ............................................................................................ S7
   cyclooctane, (Table 2, entry 10) .......................................................................................... S7
   n-octane, (Table 2, entry 11)[6] ............................................................................................. S7
   2,2-dimethylbutane, (Table 2, entry 12)[7] .......................................................................... S8
   cis-stilbene(Table2, entry 13)[8] .......................................................................................... S8
   cis-2,5-dimethyl-3-hexene-2,5-diol (Table 2, entry 14)[9] .................................................... S8
6. NMR-spectra ........................................................................................................................ S9
   trans-[Pd(H)[(IPr)(PCy)]4 .................................................................................................. S9
   1,2-diphenylethane (Table 2, entry 1) .................................................................................. S10
   1,2-diphenylpropane (Table 2, entry 2) ................................................................................ S10
   1,1-diphenylethane (Table 2, entry 3) .................................................................................. S11
   4-propylanisole (Table 2, entry 4) ....................................................................................... S11
   1-propylbenzene, (Table 2, entry 5) .................................................................................... S12
   methyl-3-phenylpropionate, (Table 2, entry 6) .................................................................. S12
   1,3-diphenylpropan-1-ol, (Table 2, entry 7) ....................................................................... S13
   cyclohexanol, (Table 2, entry 8) ........................................................................................ S13
   cyclooctene, (Table 2, entry 9) .......................................................................................... S14
   cyclooctane, (Table 2, entry 10) ........................................................................................ S14
   n-octane, (Table 2, entry 11) ............................................................................................. S15
   2,2-dimethylbutane, (Table 2, entry 12) .......................................................................... S15
   cis-stilbene(Table2, entry 13) .......................................................................................... S16
   cis-2,5-dimethyl-3-hexene-2,5-diol (Table 2, entry 14) .................................................... S16
7. References and Notes .......................................................................................................... S17
1. General considerations

All reactions were performed in dried glassware using standard Schlenk and glovebox techniques. THF, Et₂O and toluene were dispensed from a solvent purification system from Innovative Technology. Other dry solvents were obtained from commercial sources and used without further purification. [Pd(SIPr)(PCy₃)], 5, was synthesized according to the literature. All other reagents were purchased and used as received. ¹H, ¹³C {¹H} and ³¹P {¹H} Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 Ultrashield spectrometer at 298 K. Gas Chromatography analyses were performed on an Agilent 6890 apparatus equipped with a flame ionization detector and a silicon column (30 m, 320 µm, film thickness: 0.25 µm). GC-MS spectra were recorded on GC MS Agilent 5973 equipped with an Electronic Ionization chamber (E.I.). Measurement of pressure built-up was performed using Man on the Moon, Series 101 kit.

2. Dehydrogenation experiments

Experiments for gas release using [Pd(IPr)(PCy₃)]

Ammonium borane (5 mg, 0.16 mmol) and [Pd(IPr)(PCy₃)] (1.26 mg, 0.0016 mmol) were placed into the measurement vessel and solvent (2 mL) was added. The vessel was closed and heated to 50 °C for 90 min, while pressure changes were recorded using Man on the Moon, Series 101 device.
3. Kinetic experiments

Reduction of 4-Allylanisole catalyzed by SiPrPdPCy3, using AB as hydrogen source

Conversion (%)

0 10 20 30 40 50 60 70 80 90 100

0 100 200 300 400 500 600 700

Time (min.)

Conversion (IPA-d8, 50°C)

Conversion (MeOH-d4, 50°C)

Kinetic plot of reduction of 4-allyl anisole using ammonium borane

Conversion (%)

0 10 20 30 40 50 60 70 80 90 100

0 50 100 150 200 250 300

Time (min.)

Conversion of 4-Allylanisole to 4-Peptlylanisole

Formation of triisopropyl borate

Conversion of AB
4. Optimization of reaction conditions.\textsuperscript{[a]}

\[
\begin{align*}
\text{Ph} & \quad \text{Pd catalyst} \quad \text{NH}_3\text{BH}_3, 16\text{h}, 50^\circ\text{C} \quad \text{Ph} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>loading (mol%)</th>
<th>Solvent</th>
<th>GC conv.\textsuperscript{[b]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(IPr)(PCy\textsubscript{3})] 1</td>
<td>1</td>
<td>THF</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>[Pd(IPr)(PCy\textsubscript{3})] 1</td>
<td>1</td>
<td>toluene</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>[Pd(IPr)(PCy\textsubscript{3})] 1</td>
<td>1</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>&lt;5%\textsuperscript{[c]}</td>
</tr>
<tr>
<td>[Pd(IPr)(PCy\textsubscript{3})] 1</td>
<td>1</td>
<td>MeOH</td>
<td>94%</td>
</tr>
<tr>
<td>[Pd(IPr)(PCy\textsubscript{3})] 1</td>
<td>1</td>
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<td>[Pd(IPr)(PCy\textsubscript{3})] 1</td>
<td>1</td>
<td>\textsuperscript{t}PrOH</td>
<td>95%</td>
</tr>
<tr>
<td>[Pd(IPr)(PCy\textsubscript{3})] 1</td>
<td>0.1</td>
<td>\textsuperscript{t}PrOH</td>
<td>95%</td>
</tr>
<tr>
<td>[Pd(IPr)(PCy\textsubscript{3})] 1</td>
<td>0.05</td>
<td>MeOH</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>[Pd(IPr)(PCy\textsubscript{3})] 1</td>
<td>0.05</td>
<td>EtOH</td>
<td>70%</td>
</tr>
<tr>
<td>[Pd(IPr)(PCy\textsubscript{3})] 1</td>
<td>0.05</td>
<td>\textsuperscript{t}PrOH</td>
<td>88%\textsuperscript{[d]}</td>
</tr>
<tr>
<td>[Pd(SiPr)(PCy\textsubscript{3})] 5</td>
<td>0.05</td>
<td>\textsuperscript{t}PrOH</td>
<td>99%</td>
</tr>
<tr>
<td>[Pd(IPr)(PPh\textsubscript{3})] 6</td>
<td>0.05</td>
<td>\textsuperscript{t}PrOH</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>[Pd(SiPr)(PPh\textsubscript{3})] 7</td>
<td>0.05</td>
<td>\textsuperscript{t}PrOH</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>[Pd(IPr)\textsubscript{2}]\textsubscript{8}</td>
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<td>\textsuperscript{t}PrOH</td>
<td>25%</td>
</tr>
<tr>
<td>[Pd(IPr)(PAd\textsubscript{2}nBu)]\textsubscript{9}</td>
<td>0.05</td>
<td>\textsuperscript{t}PrOH</td>
<td>60%</td>
</tr>
<tr>
<td>Pd/C</td>
<td>0.05</td>
<td>\textsuperscript{t}PrOH</td>
<td>N.R.</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Reaction conditions: trans-stilbene (0.5 mmol), catalyst, NH\textsubscript{3}BH\textsubscript{3} (1 eq.), solvent (1 mL), 50ºC, 16 h. \textsuperscript{[b]} Conversion, determined by GC, average of at least two runs. \textsuperscript{[c]} Reaction carried out at 40ºC. \textsuperscript{[d]} No reaction occurred at rt.

5. Hydrogenation

5.1 Typical procedure for the hydrogenation of alkenes

In a glovebox, a 25 mL Schlenk flask fitted with a septum and equipped with a magnetic stirring bar was charged with the unsaturated compound (0.50 mmol), ammonia borane (0.25 mmol), isopropanol (1 mL) and catalyst (147 µL of 0.0017 M solution in isopropanol). The reaction mixture was stirred under an argon atmosphere at 50 ºC for 16 h. Removal of the solvent in vacuo followed by flash column chromatography furnished the resulting product. For volatile compounds, the yield was measured as a NMR-yield with 4-bromoanisole or 1,3,5-trimethoxybenzene as internal standards.
**1,2-diphenylethane (Table 2, entry 1)**

The procedure afforded, after flash chromatography on silica gel (pentane), 91 mg (0.50 mmol, 99%) of the title compound.

$^1$H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.30–7.26 (m, 4 H), 7.21–7.17 (m, 6 H), 2.92 (s, 4 H). $-^{13}$C-$^1$H NMR (CDCl$_3$, 100 MHz) δ (ppm) = 141.8, 128.5, 128.4, 125.9, 38.0.

**1,2-diphenylpropane (Table 2, entry 2)**

The procedure afforded, after flash chromatography on silica gel (pentane), 82 mg (0.42 mmol, 88%) of the title compound.

$^1$H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.46–7.32 (m, 8 H), 7.25 (d, $J_{HH} = 7.0$ Hz, 2 H), 3.21–3.09 (m, 2 H), 2.94 (dd, $J_{HH} = 12.8$ Hz, $J_{HH} = 7.8$ Hz, 1 H), 1.41 (d, $J_{HH} = 6.8$ Hz, 3 H). $-^{13}$C-$^1$H NMR (CDCl$_3$, 100 MHz) δ (ppm) = 147.1, 140.9, 129.3, 128.5, 128.3, 127.2, 126.2, 126.0, 45.2, 42.0, 21.3.

**1,1-diphenylethane (Table 2, entry 3)**

The procedure afforded, after flash chromatography on silica gel (pentane), 91 mg (0.49 mmol, 99%) of the title compound.

$^1$H NMR (CDCl$_3$, 400 MHz) δ (ppm) = 7.26 (dd, $J_{HH} = 7.1$ Hz, $J_{HH} = 7.6$ Hz, 4 H), 7.20 (d, $J_{HH} = 7.1$ Hz, 4 H), 7.15 (dd, $J_{HH} = 7.6$ Hz, $J_{HH} = 7.6$ Hz, 2 H), 4.13 (q, $J_{HH} = 7.3$ Hz, 1 H), 1.62 (d, $J_{HH} = 7.3$ Hz, 3 H). $-^{13}$C-$^1$H NMR (CDCl$_3$, 100 MHz) δ (ppm) = 146.5, 128.5, 127.7, 126.1, 44.9, 22.0.

**4-propylanisole (Table 2, entry 4)**

The procedure afforded 74 mg (0.50 mmol, 99%) of the title compound.

$^1$H NMR (isopropanol-$d_8$, 400 MHz) δ (ppm) = 7.96 (d, $J_{HH} = 8.1$ Hz, 2 H), 7.71 (d, $J_{HH} = 8.1$ Hz, 2 H), 4.65 (s, 3 H), 3.44 (t, $J_{HH} = 7.4$ Hz, 2 H), 2.54 (qt, $J_{HH} = 7.3$ Hz, $J_{HH} = 7.4$ Hz, 2 H), 1.86 (t, $J_{HH} = 7.3$ Hz, 3 H). $-^{13}$C-$^1$H NMR (isopropanol-$d_8$, 100 MHz) δ (ppm) = 158.6, 135.2, 129.9, 114.4, 55.5, 38.0, 25.6, 14.2.

**1-propylbenzene, (Table 2, entry 5)**

The procedure afforded 39 mg (0.33 mmol, 78%) of the title compound.

$^1$H NMR (isopropanol-$d_8$, 400 MHz) δ (ppm) = 8.15 (dd, $J_{HH} = 7.3$ Hz, $J_{HH} = 7.6$ Hz, 2 H), 8.06–8.5 (m, 3 H), 3.50 (t, $J_{HH} = 7.3$ Hz, 2 H), 2.58 (qt, $J_{HH} = 7.3$ Hz, $J_{HH} = 7.3$ Hz, 2 H), 1.88 (t, $J_{HH} = 7.3$ Hz, 3 H). $-^{13}$C-$^1$H NMR (isopropanol-$d_8$, 100 MHz) δ (ppm) = 142.9, 129.0, 128.9, 126.3, 38.9, 25.4, 14.2.
methyl-3-phenylpropionate, (Table 2, entry 6)

The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 10:1), 80 mg (0.49 mmol, 98%) of the title compound.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) = 7.37–7.34 (m, 2 H), 7.29–7.26 (m, 3 H), 3.74 (s, 3 H), 3.03 (t, $J_{HH} = 8.2$ Hz, 2 H), 2.71 (t, $J_{HH} = 8.2$ Hz, 2 H). $-^{13}$C-$^1$H NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) = 173.3, 140.6, 128.6, 126.3, 51.6, 35.7, 31.0.

1,3-diphenylpropan-1-ol, (Table 2, entry 7)

The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 10:1), 104 mg (0.49 mmol, 98%) of the title compound.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm) = 7.43–7.40 (m, 4 H), 7.36–7.33 (m, 3 H), 7.17–7.16 (m, 3 H), 4.72 (t, $J_{HH} = 6.6$ Hz, 1 H), 2.84–2.68 (m, 2 H), 2.23–2.04 (m, 3 H). $-^{13}$C-$^1$H NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) = 144.7, 141.9, 128.6, 128.5, 128.45, 127.7, 126.0, 125.9, 73.9, 40.5, 32.1.

cyclohexanol, (Table 2, entry 8)

The procedure afforded 49 mg (0.49 mmol, 97%) of the title compound.

$^1$H NMR (isopropanol-$d_8$, 400 MHz) $\delta$ (ppm) = 4.49 (m, 1 H), 2.86–2.85 (m, 2 H), 2.70–2.68 (m, 2 H), 2.49 (d, $J_{HH} = 11.7$ Hz, 1 H), 2.07 (m, 6 H). $-^{13}$C-$^1$H NMR (isopropanol-$d_8$, 100 MHz) $\delta$ (ppm) = 70.2, 36.1, 26.5, 25.1.

cyclooctene, (Table 2, entry 9)

$^1$H NMR (solvent, 400 MHz) $\delta$ (ppm) 6.60-6.53 (m, 2 H) 3.15-3.05 (m, 4 H) 2.5-2.4 (m, 8 H).

cyclooctane, (Table 2, entry 10)

The procedure afforded 55 mg (0.50 mmol, >99%) of the title compound.

$^1$H NMR (MeOH-$d_4$, 400 MHz) $\delta$ (ppm) = 1.54 (s, 16 H). $-^{13}$C-$^1$H NMR (MeOH-$d_4$, 100 MHz) $\delta$ (ppm) = 26.8.

n-octane, (Table 2, entry 11)

The procedure afforded 46 mg (0.40 mmol, 80%) of the title compound.

$^1$H NMR (isopropanol-$d_8$, 400 MHz) $\delta$ (ppm) = 2.25 (bs, 12 H), 1.88–1.84 (m, 6 H). $-^{13}$C-$^1$H NMR (isopropanol-$d_8$, 100 MHz) $\delta$ (ppm) = 31.8, 29.1, 22.4, 13.5.
2,2-dimethylbutane, (Table 2, entry 12)\textsuperscript{12}

The procedure afforded 30 mg (0.35 mmol, 69\%) of the title compound.
\(^1\)H NMR (isopropanol-\textit{d}_8, 400 MHz) \(\delta\) (ppm) = 1.22 (q, \(J_{HH} = 7.3\) Hz, 2 H), 0.86 (s, 9 H), 0.83 (t, \(J_{HH} = 7.3\) Hz, 3 H). \(^{13}\)C-\{\(^1\)H\} NMR (isopropanol-\textit{d}_8, 100 MHz) \(\delta\) (ppm) = 38.3, 32.0, 30.5, 10.4.

\textit{cis}-stilbene (Table 2, entry 13)\textsuperscript{13}

The procedure afforded, after flash chromatography on silica gel (hexane), 80 mg (0.44 mmol, 88\%) of the title compound.
\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\) (ppm) = 7.26–7.16 (m, 10 H), 6.56 (s, 2 H). \(^{13}\)C-\{\(^1\)H\} NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\) (ppm) = 137.3, 130.3, 128.9, 128.2, 127.1.

\textit{cis}-2,5-dimethyl-3-hexene-2,5-diol (Table 2, entry 14)\textsuperscript{14}

The procedure afforded 55 mg (0.38 mmol, 76\%) of the title compound.
\(^1\)H NMR (methanol-\textit{d}_4, 400 MHz) \(\delta\) (ppm) = 5.29 (s, 2 H), 1.38 (s, 12 H). \(^{13}\)C-\{\(^1\)H\} NMR (methanol-\textit{d}_4, 100 MHz) \(\delta\) (ppm) = 132.3, 71.1, 31.1.
6. NMR-spectra

trans-[Pd(H)\textsubscript{2}(IPr)(PCy\textsubscript{3})] 4
1,2-diphenylethane (Table 2, entry 1)

1,2-diphenylpropane (Table 2, entry 2)
1,1-diphenylethane (Table 2, entry 3)

4-propylanisole (Table 2, entry 4)
1-propylbenzene, \((Table\ 2,\ entry\ 5)\)

\[
\text{Ph}\text{-propylbenzene}
\]

methyl-3-phenylpropionate, \((Table\ 2,\ entry\ 6)\)

with \(p\)-bromoanisole as internal standard
1,3-diphenylpropan-1-ol, (Table 2, entry 7)

![1,3-diphenylpropan-1-ol spectrum](image1)

cyclohexanol, (Table 2, entry 8)

![cyclohexanol spectrum](image2)
**cyclooctene, (Table 2, entry 9)**

![Graph of cyclooctene spectrum]

**cyclooctane, (Table 2, entry 10)**

![Graph of cyclooctane spectrum]
n-octane, (Table 2, entry 11)

2,2-dimethylbutane, (Table 2, entry 12)
cis-stilbene (Table 2, entry 13)

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\]

cis-2,5-dimethyl-3-hexene-2,5-diol (Table 2, entry 14)

\[
\begin{array}{c}
\text{HO} \\
\text{OH}
\end{array}
\]
7. References and Notes