Supporting Information

Structurally Versatile Ligand System for the Ruthenium Catalyzed One-Pot Hydrogenation of CO$_2$ to Methanol

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1. General information.............................................................................................2
2. Synthesis of (tdppcy)Ru(tmm) ...........................................................................2
3. Analysis of Reaction Mixtures...........................................................................3
  3.1. Analysis of a Post-Reaction Mixture ...............................................................3
  3.2. Formation of (tdppcy)(PPh$_3$)$_2$Ru(H)$_2$ under catalytic reaction conditions .................................................................5
  3.3. Analysis of a Post-Reaction Mixture without CO$_2$ .........................................6
4. Catalytic Transformation of Carbon Dioxide ....................................................8
  4.1. Typical procedure for in-situ reaction with ruthenium precursor, tdppcy ligand and acid co-catalyst .................................................................8
  4.2. Typical procedure for reactions with (PPh$_3$)$_2$Ru(H)$_2$, tdppcy ligand and acid co-catalyst in a biphasic mixture ........................................................................12
  4.3. Typical procedure for catalytic reaction with (tdppcy)Ru(tmm) and Al(OTf)$_3$ .................................................................14
5. Calculation of Initial Activity TOF$_{ini}$..................................................................14
1. General information

Safety advice: High-pressure experiments with compressed gases represent a significant safety risk and must be conducted only following appropriate safety procedures and in conjunction with the use of suitable equipment.

For complex synthesis and catalytic experiments, moisture and oxygen were excluded by working in a glovebox or by using Schlenk techniques. Argon 4.8 (Messer, Germany) was used as inert gas. Glassware was dried in an oven at 100 °C followed by heating under vacuum and refilling with argon at least three times. All solvents were purified by distillation prior to use. Tetrahydrofuran (THF) was degassed by bubbling argon with a frit, dried by passing over activated alumina in steel columns and stored over molecular sieve. All alcohols used were degassed by distillation under argon and dried as received unless stated otherwise. Reaction gases hydrogen (5.0) and carbon dioxide (4.6) were supplied by Linde and PraxAir and used without further purification.

cis,cis-1,3,5-cyclohexanetritosylate and cis,cis-1,3,5-tris(diphenylphosphino)cyclohexane (tdppcy) were synthesized by literature procedures.

1H-NMR-spectra were recorded on Bruker AV600, AV400 or AV300 spectrometer at room temperature. Chemical shifts \( \delta \) are given in ppm relative to tetramethylsilane (\(^1\)H and \(^13\)C) and 85% phosphoric acid (\(^31\)P). First order spin multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quadruplet (qua), quintet (qui), sextet (sext) and septet (sep). Couplings of higher order or overlapped signals are denoted as multiplet (m), broadened signals as (br. s). First order coupling constants \( J \) are given in Hz. Assignments are based on attached proton tests (ATP) and 2-D correlation spectroscopy (HSQC, HMQC, HMBC). ESI-MS were performed using a Varian-MS-500 LC/MS.

GC analysis of the gas phase was performed on a HP 6890 chromatograph with a 2 m ShinCarbon ST (100/120 mesh) column with TCD detection using ethylene (99.95%) as internal standard.

2. Synthesis of (tdppcy)Ru(tmm)

Bis(2-methylallyl)(2,5-cyclooctadiene)ruthenium(II) (0.100 g, 0.314 mmol) and tdppcy (3, 0.200 g, 0.314 mmol, 1 equiv.) were weighed in a Schlenk tube and suspended in mesitylene (8 mL). The reaction mixture was heated to 140 °C for 1 h. Upon cooling to room temperature a brownish solid precipitated, addition of \( n \)-pentane (10 mL) led to the formation of additional brownish solid. Filtration of the solid followed by washing with \( Et_2O \) (2 x 8 mL) and THF (5 mL) afforded a slightly off-white solid. Drying in vacuo yielded analytically pure (tddpcy)Ru(tmm) in a moderate yield (53%).

\(^1\)H-NMR (400 MHz, \( CD_2Cl_2 \)): \( \delta = 1.64 \) (s, 6H, tmm-\( CH_2 \)), 2.06 - 2.19 (m, 3H, \( CHH_3 \)), 2.29 - 2.57 (m, 3H, \( PCH \)), 2.79 - 2.91 (m, 3H, \( CH_2H \)), 6.94 (t, \(^3J(C,H) = 7.5\) Hz, 12H, Ar-\( H \)), 6.97 - 7.05 (m, 18H, Ar-\( H \)) ppm; \(^13\)C\(^{(1)}\)H-NMR (151 MHz, \( CD_2Cl_2 \)): \( \delta = 28.7-29.0 \) (m, C-\( 1 \)-cy), 30.2 (t, \(^2J(PC) = 5.5\) Hz, C-\( 2 \)-cy), 44.2 - 44.9 (m, tmm-\( CH_2 \)), 105.7 (s, tmm-\( C \)), 127.6 - 127.7 (m, \( \alpha -C_6H_5 \)), 128.2 (s, \( p-C_6H_5 \)), 133.1 - 133.2 (m, \( o -C_6H_5 \)), 141.8 - 142.5 (m, ipso-\( C_5H_6 \)) ppm; \(^31\)P\(^{(1)}\)H-NMR (161 MHz, \( CD_2Cl_2 \)): \( \delta = 38.31 \) (m, 3P) ppm; HRMS (ESI+): \( C_{46}H_{45}P_3Ru [M + H]^+ \): Calc: 793.186 m/z, Found: 793.186 m/z.

Figure S1: \(^1\)H-NMR-spectrum (400 MHz, \( CD_2Cl_2 \)) of (tdppcy)Ru(tmm).
3. Analysis of Reaction Mixtures

3.1. Analysis of a Post-Reaction Mixture

(tdppcy)Ru(tmm) (15.8 mg, 20 µmol) and Al(OTf)$_3$ (75.9 mg, 160 µmol, 8 equiv.) were weighed in a glass inset and transferred to a stainless-steel autoclave. Ethanol (4 mL) was added via syringe and the autoclave was pressurized at room temperature with CO$_2$ (30 bar), followed by hydrogen to a total pressure of 120 bar. The reaction mixture was stirred and heated to 120 °C in an aluminium heating cone for 20 h. After the reaction time, the autoclave was cooled to room temperature and then carefully vented via a Schlenk line. The reaction mixture was transferred into a Schlenk tube and dried in vacuo. The yellow-orange residue was dissolved in CDCl$_3$ and analysed by NMR and IR. $^1$H-NMR-spectroscopy showed a single, characteristic hydride pattern comparable with similar tripodal biscarbonyl complexes. The $^{31}$P-NMR-spectrum clearly hinted towards the formation of the biscarbonyl species with the characteristic doublet and triplet pattern (Figure S4).
Figure S4: $^{31}$P($^1$H)-NMR-spectrum (161 MHz, CDCl$_3$) of the post-catalytic residue.

Compared to the observed [(Triphos)RuH(CO)$_2$]$^+$ ($\delta = 18.6$ (d, $J_{PP} = 28.7$ Hz, 2P), 6.3 (t, $J_{PP} = 28.7$ Hz, 1P) ppm) by Klankermayer and Leitner, the pattern slightly shifts. ATR-IR measurements of the residue furthermore show characteristic patterns for carbonyl ligands at the ruthenium centre (Figure S5). Furthermore, strong resonances of the triflate are clearly visible.$^3$

Figure S5: ATR-IR-spectrum of the post-catalytic residue.

$[(tdppcy)RuH(CO)$_2$]$^+$ seems to resemble the only complex formed after catalysis (Scheme S1).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = -6.59$ (dt, $^2J_{PH-trans} = 65.8$ Hz, $^2J_{PH-cis} = 15.2$ Hz, 1H, Ru-H) ppm; $^{31}$P($^1$H)-NMR (161 MHz, CDCl$_3$): $\delta = 16.2$ (d, $^2J_{PP} = 26.6$ Hz, 2P), 10.1 (t, $^2J_{PP} = 26.6$ Hz, 1P) ppm; ATR-IR (cm$^{-1}$): 2045.4, 1979.5 (CO).
3.2. Formation of (tdppcy)(PPh₃)Ru(H)₂ under catalytic reaction conditions

(PPh₃)₄Ru(H)₂ (11.5 mg, 10 μmol) and tdppcy (6.4 mg, 10 μmol, 1.0 equiv.) were weighed in a glass inset and transferred to a stainless-steel autoclave. THF-d₈ (1 mL) was added via syringe and the autoclave was pressurized with H₂ (80 bar) at room temperature. The mixture was stirred at 120 °C in an aluminum cone for 4 hours. Afterwards, the autoclave was cooled to room temperature and was carefully vented via a Schlenk line. The brownish solution was analysed by NMR-spectroscopy without further purification. The ¹H-NMR and ³¹P(¹H)-NMR spectra revealed unreacted (PPh₃)₄Ru(H)₂ and tdppcy, as well as characteristic signals resembling the formation of (tdppcy)(PPh₃)Ru(H)₂ (Figure S6-S8).⁴

Figure S6: ¹H-NMR-spectrum (a) and ¹H(³¹P)-NMR-spectrum (b) (400 MHz, THF-d₈) of the hydride region.

Figure S7: ³¹P(¹H)-NMR-spectrum (161 MHz, THF-d₈) of the reaction mixture.
Figure S8: $^{31}$P{$^1$H}-NMR-spectrum (161 MHz, THF-$d_8$). Spectrum from 26 to 55 ppm. A characteristic set of signals can be assigned to (tdppcy)(PPh$_3$)Ru(H)$_2$ and confirms the formation under catalytic conditions. $\delta = 53.36$ (dt, $^2J_{PP} = 221.4$ Hz, $^2J_{PPh_3} = 25.7$ Hz, 1P, PPh$_3$), 46.43 (dt, $^2J_{PPh_3} = 221.8$ Hz, $^2J_{PP} = 14.9$ Hz, 1P, P$_{trans}$), 28.11 (dd, $^2J_{PP} = 25.7$ Hz, $^2J_{PP} = 14.9$ Hz, 2P, P$_{cis}$). 

3.3. Analysis of a Post-Reaction Mixture without CO$_2$

(tdppcy)Ru(tmm) (7.9 mg, 10 µmol) and Al(OTf)$_3$ (9.5 mg, 20 µmol, 2.0 equiv.) were weighed in a glass inset and transferred to a stainless-steel autoclave. THF (2 mL) was added via syringe and the autoclave was pressurized at room temperature with H$_2$ (120 bar). The reaction mixture was stirred and heated to 120 °C in an aluminium heating cone for 20 h. After the reaction time, the autoclave was cooled to room temperature and then carefully vented. The reaction mixture was analysed by NMR-spectroscopy without further isolation. The $^{31}$P{$^1$H} exhibits a single resonance ($\delta = 34.5$ ppm), whereas the missing signals in the hydride region of the $^1$H-NMR-spectrum hint for a species other than a hydrido-bridged dimeric complex of the type [(tdppcy)RuH]$_2$ or [((tdppcy)Ru)$_2$(H)]OTf (Figure S9).

A separate reaction was carried out to test the possible in-situ formation of a (tdppcy)Ru$^{2+}$ species under the CO$_2$-free reaction conditions. To a solution of (tdppcy)Ru(tmm) (7.9 mg, 10 µmol) in THF-$d_8$ (0.5 mL), HNTf$_2$ (5.6 mg, 20 µmol, 2.0 equiv.) was added and the resulting solution was analysed by NMR-spectroscopy. This experiment resulted in the observation of a single resonance in the $^{31}$P{$^1$H}-NMR-spectrum ($\delta = 42.5$ ppm, Figure S10) that is slightly shifted in comparison to the complex obtained in the CO$_2$-free reaction conditions.
Figure S9: $^{31}$P($^1$H)-NMR-spectrum (a) (161 MHz, DMSO-$d_6$) of the reaction mixture without CO$_2$ and $^1$H-NMR-spectrum (b) (400 MHz, DMSO-$d_6$) of the hydride region.

Figure S10: $^{31}$P($^1$H)-NMR-spectrum (161 MHz, DMSO-$d_6$) of the reaction mixture of (tdppcy)Ru(tmm) with 2 equiv. of HNTi$_2$ in THF-$d_8$ as solvent.
4. Catalytic Transformation of Carbon Dioxide

4.1. Typical procedure for *in-situ* reaction with ruthenium precursor, tdppcy ligand and acid co-catalyst

In a typical experiment, under an argon atmosphere, an autoclave glass inset equipped with a magnetic stirring bar was charged with the ruthenium precursor \((\text{PPh}_3)_4\text{Ru(H)}_2\) (11.5 mg, 10 µmol), the tdppcy ligand (1.1 equiv.) and acid co-catalyst (2 equiv.). The glass inset was transferred to a stainless-steel autoclave and the solvent (4 mL) was added via syringe. The autoclave was pressurized at room temperature with CO\(_2\) to the respective pressure (typically 30 bar), followed by hydrogen to the indicated total pressure (typically 120 bar). The reaction mixture was stirred and heated to the respective reaction temperature in an aluminium heating cone. After the reaction time of 20 h, the autoclave was cooled to room temperature and then carefully vented. Mesitylene was added as internal standard and the resulting solution analysed by \(^1\text{H}\)-NMR-spectroscopy (Figures S6 and S7). In cases of deviating parameters, solvents, acidic additives or triphos as ligand the procedure remained the same. TONs were found to be reproducible within \(\Delta\text{TON} = \pm 5\%\) in at least two independent runs in selected experiments.

**Figure S11**: Exemplary \(^1\text{H}\)-NMR-spectrum (300 MHz, DMSO-\(d_6\)) for the hydrogenation of CO\(_2\) to MeOH in THF as solvent.

**Figure S12**: Exemplary \(^{13}\text{C}\)-APT-NMR-spectrum (75 MHz, DMSO-\(d_6\)) for the hydrogenation of CO\(_2\) to MeOH in THF as solvent.
Figure S13: Exemplary $^1$H-NMR-spectrum (300 MHz, DMSO-$d_6$) for the hydrogenation of CO$_2$ to MeOH in EtOH as solvent.

Figure S14: Exemplary $^{13}$C-APT-NMR-spectrum (75 MHz, DMSO-$d_6$) for the hydrogenation of CO$_2$ to MeOH in EtOH as solvent.
Figure S15: Exemplary GC analysis of the gas phase for the catalytic hydrogenation of CO\textsubscript{2} to MeOH in EtOH as solvent.
resulted in a strong increase of the corresponding MeOH peak (49 ppm) in the enriched CO.

In case of \( \text{H}_\text{p} = 1500 \text{ rpm.} \) [f] without tdppcy [g] spectroscopy with mesitylene as internal standard. [c] stirring speed = 500 rpm. [d] stirring speed = 1000 rpm. [e] stirring speed = 1500 rpm. [a] tdppcy = 1.1 equiv., \( V_{\text{solvent}} = 4 \text{ mL}, \ p(\text{H}_2/\text{CO}_2) \ [\text{bar/bar}] = 90/30 \text{ at r.t., } t = 20 \text{ h.} \) [b] TONs determined by \( ^1\text{H}-\text{NMR-} \)
spectroscopy with mesitylene as internal standard. [c] stirring speed = 500 rpm. [d] stirring speed = 1000 rpm. [e] stirring speed = 1500 rpm. [f] without tdppcy [g] \( p(\text{H}_2/\text{CO}_2) \ [\text{bar/bar}] = 120/0 \text{ at r.t.} \) [h] \( p(\text{H}_2/\text{CO}_2) \ [\text{bar/bar/bar}] = 90/8/22. \)

In case of \(^{13}\text{C}\)-enriched \( \text{CO}_2 \) (Table S1, entry 23), \(^{13}\text{CO}_2 \) was pressurized to 8 bar, followed by non-enriched \( \text{CO}_2 \) to a total of 30 bar. Then hydrogen was pressurized to a total of 120 bar. The reaction resulted in a strong increase of the corresponding MeOH peak (49 ppm) in the \(^{13}\text{C}\)-NMR (Figure S15).

![Figure S16: \(^{13}\text{C}\)-APT-NMR (75 MHz, DMSO-\( d_6 \)): I) 8 bar of \(^{13}\text{CO}_2 \) is used. II) without \(^{12}\text{C} \) enriched \( \text{CO}_2 \).](image)
Table S2: Comparison of catalyst systems bearing the tdppcy or Triphos ligand for the hydrogenation of carbon dioxide to methanol.\(^{[a]}\)

<table>
<thead>
<tr>
<th>#</th>
<th>Ligand</th>
<th>Solvent</th>
<th>(T) [°C]</th>
<th>TON(_{\text{MeOH}})(^{[b]})</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Triphos</td>
<td>THF</td>
<td>120</td>
<td>232</td>
</tr>
<tr>
<td>2</td>
<td>tdppcy</td>
<td>THF</td>
<td>120</td>
<td>542</td>
</tr>
<tr>
<td>3(^{[c]})</td>
<td>Triphos</td>
<td>THF</td>
<td>120</td>
<td>249</td>
</tr>
<tr>
<td>4(^{[c]})</td>
<td>tdppcy</td>
<td>THF</td>
<td>120</td>
<td>609</td>
</tr>
<tr>
<td>5</td>
<td>Triphos</td>
<td>EtOH</td>
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<td>566</td>
</tr>
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<td>EtOH</td>
<td>120</td>
<td>968</td>
</tr>
<tr>
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<td>EtOH</td>
<td>120</td>
<td>686</td>
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<tr>
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<td>Triphos</td>
<td>2-MTHF</td>
<td>120</td>
<td>100</td>
</tr>
<tr>
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<td>2-MTHF</td>
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<td>69</td>
</tr>
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<td>(tdppcy)Ru(tmm)</td>
<td>THF</td>
<td>120</td>
<td>1104</td>
</tr>
<tr>
<td>12(^{[d]})</td>
<td>(tdppcy)Ru(tmm)</td>
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<td>1202</td>
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<td>THF</td>
<td>120</td>
<td>182</td>
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<td>14(^{[c]})</td>
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<td>THF</td>
<td>120</td>
<td>252</td>
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<td>EtOH</td>
<td>120</td>
<td>1118</td>
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<td>16(^{[c]})</td>
<td>(tdppcy)Ru(tmm)</td>
<td>EtOH</td>
<td>120</td>
<td>2148</td>
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<tr>
<td>17</td>
<td>(triphos)Ru(tmm)</td>
<td>EtOH</td>
<td>120</td>
<td>581</td>
</tr>
<tr>
<td>18(^{[c]})</td>
<td>(triphos)Ru(tmm)</td>
<td>EtOH</td>
<td>120</td>
<td>528</td>
</tr>
</tbody>
</table>

\(^{[a]}\) for in-situ system: (PPh\(_3\))\(_4\)Ru(H)\(_2\) = 10 µmol, 1.1 equiv. ligand, 2.0 equiv. Al(O(Tf))\(_3\), for preformed catalysts: [Ru] = 5 µmol, 1.0 equiv. Al(O(Tf))\(_3\); \(V_{\text{solvent}} = 4 \, \text{mL}, p(H/CO\(_2\)) \text{bar/bar} \approx 90/30 \text{ at r.t., } t = 20 \, \text{h}.\(^{[b]}\) TONs determined by \(^{1}\)H-NMR-spectroscopy with mesitylene as internal standard. \(^{[c]}\) [Ru] = 5 µmol, Al(O(Tf))\(_3\) = 40 µmol (8 equiv.). \(^{[d]}\) \(t = 72 \, \text{h}.\)

4.2. Typical procedure for reactions with (PPh\(_3\))\(_4\)Ru(H)\(_2\), tdppcy ligand and acid co-catalyst in a biphasic mixture

In a typical experiment, under an argon atmosphere, an autoclave glass inset equipped with a magnetic stirring bar was charged with the ruthenium precursor (PPh\(_3\))\(_4\)Ru(H)\(_2\) (11.5 mg, 10 µmol), the tdppcy ligand (1.1 equiv.) and acid co-catalyst (2 equiv.). The glass inset was transferred to a stainless-steel autoclave and the alcohol (2 mL) was added via syringe, followed by degassed water (2 mL). The autoclave was pressurized at room temperature with CO\(_2\) to the respective pressure (typically 30 bar), followed by hydrogen to the indicated total pressure (typically 120 bar). The reaction mixture was stirred and heated to the respective reaction temperature in an aluminium heating cone. After the reaction time of 20 h, the autoclave was cooled to room temperature and then carefully vented under argon via a Schlenk-line. The reaction mixture was transferred into a Schlenk-flask and the phases were separated. The organic phase was transferred into a fresh autoclave equipped with a glass inset and magnetic stirring bar. Water (2 mL) added and catalysis repeated as described before. The aqueous phase was utilized for analysis. Acetone was added as internal standard and the resulting solution analysed by \(^{1}\)H-NMR-spectroscopy. TONs were found to be reproducible within \(\Delta\text{TON} = \pm 5\%\) in at least two independent runs in selected experiments.

Figure S12 and S13 show examples of a \(^{1}\)H- and \(^{13}\)C-NMR-spectrum for the biphasic mixture of \(n\)-octanol and water. No other alcohol contaminant except for methanol could be detected and similar behavior can be observed using \(n\)-decanol and water.
Figure S17: Exemplary $^1$H-NMR-spectrum (400 MHz, DMSO-$d_6$) of the aqueous phase for the hydrogenation of CO$_2$ to MeOH in the biphasic mixture with $n$-octanol/H$_2$O as biphasic system.

Figure S18: Exemplary $^{13}$C-APT-NMR-spectrum (100 MHz, DMSO-$d_6$) of the aqueous phase for the hydrogenation of CO$_2$ to MeOH in the biphasic mixture with $n$-octanol/H$_2$O as biphasic system.
4.3. Typical procedure for catalytic reaction with (tdppcy)Ru(tmm) and Al(OTf)₃

In a typical experiment, under an argon atmosphere, an autoclave glass inset equipped with a magnetic stirring bar was charged with (tdppcy)Ru(tmm) (7.9 mg, 10 µmol) and Al(OTf)₃ (4.7 mg, 10 µmol, 1 equiv.). The glass inset was transferred to a stainless-steel autoclave and the solvent (4 mL) was added via syringe.

The autoclave was pressurized at room temperature with CO₂ to the respective pressure (typically 30 bar), followed by hydrogen to the indicated total pressure (typically 120 bar). The reaction mixture was stirred and heated to the respective reaction temperature in an aluminium heating cone. After the reaction time of 20 h, the autoclave was cooled to room temperature and then carefully vented. Mesitylene was added as internal standard and the resulting solution analysed by ¹H-NMR-spectroscopy.

In cases of deviating parameters, solvents or acidic additives or (triphos)Ru(tmm) the procedure remained the same. TONs were found to be reproducible within ΔTON = ±5% in at least two independent runs in selected experiments.

Table S3: Additional parameter variation of the (tdppcy)Ru(tmm) catalyst system in the hydrogenation of CO₂ to methanol.[a]

<table>
<thead>
<tr>
<th>#</th>
<th>[Ru] [µmol]</th>
<th>Acid [equiv.]</th>
<th>Solvent</th>
<th>T [°C]</th>
<th>TONMeOH[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1[c]</td>
<td>(tdppcy)Ru(tmm) [2.5]</td>
<td>Al(OTf)₃ [1]</td>
<td>THF</td>
<td>120</td>
<td>1186</td>
</tr>
<tr>
<td>2[c]</td>
<td>(tdppcy)Ru(tmm) [2.5]</td>
<td>Al(OTf)₃ [1]</td>
<td>EtOH</td>
<td>120</td>
<td>1511</td>
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<tr>
<td>4.2[f]</td>
<td>(tdppcy)Ru(tmm) [10]</td>
<td>Al(OTf)₃ [2]</td>
<td>2-MTHF</td>
<td>120</td>
<td>274</td>
</tr>
<tr>
<td>4.3[g]</td>
<td>(tdppcy)Ru(tmm) [10]</td>
<td>Al(OTf)₃ [2]</td>
<td>2-MTHF</td>
<td>120</td>
<td>112</td>
</tr>
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</table>

[a] V_Solvent = 4 mL, p(H₂/CO₂) [bar/bar] = 90/30 at r.t., t = 20 h. [b] TONs determined by ¹H-NMR-spectroscopy with mesitylene as internal standard. [c] t = 72 h. [d] p(H₂/CO₂) [bar/bar] = 30/50 at r.t. [e] Extraction of organic phase with degassed water (2 mL) after catalysis. TON obtained by analysis of aqueous phase with acetone as internal standard. [f] Reuse of organic phase of run 4.1. Extraction of organic phase with degassed water (2 mL) after catalysis. TON obtained by analysis of aqueous phase with acetone as internal standard. [g] Reuse of organic phase of run 4.2. Extraction of organic phase with degassed water (2 mL) after catalysis. TON obtained by analysis of aqueous phase with acetone as internal standard.

5. Calculation of Initial Activity TOFₗⁱⁿ

For the determination of the initial TOF, a linear regression was fitted to experimental data to obtain the initial slope (Figure S14). n_MeOH was determined by ¹H-NMR spectroscopy using mesitylene as internal standard. An exemplary calculation of the initial TOF is shown in equation 1.1 to 1.3. Selected experimental and calculated data are given in Table S4.

\[
\frac{n_{\text{MeOH}}}{\Delta p} = \frac{5.80 \text{ mmol}}{72.3 \text{ bar}} = 8.03 \cdot 10^{-2} \text{ mmol/bar} \tag{1.1}
\]

\[
m_n = - m_{\Delta p} \frac{n_{\text{MeOH}}}{\Delta p} \times 8.03 \cdot 10^{-2} \text{ mmol/bar} = 6.27 \cdot 10^{-4} \text{ mmol/s} \tag{1.2}
\]

\[
\text{TOF}_{\text{Ini}} = \frac{m_n}{m_{\text{cat}}} = \frac{6.27 \cdot 10^{-4} \text{ mmol/s}}{0.005 \text{ mmol}} = 0.127 \approx 458 \text{ h}^{-1} \tag{1.3}
\]
Figure S19: Exemplary pressure drop curve for the catalytic hydrogenation of CO$_2$ to MeOH in EtOH as solvent.

Table S4: Selected experimental and calculated data for the initial activity (TOF$_{ini}$) in the hydrogenation of CO$_2$ to methanol.[a]

<table>
<thead>
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<th>#</th>
<th>Precatalyst</th>
<th>Acid</th>
<th>Solvent</th>
<th>$\Delta p$ [bar]</th>
<th>$m_{\Delta p}$ [mbar s$^{-1}$]</th>
<th>$n_{\text{MeOH}}$ [mmol][b]</th>
<th>TOF$_{ini}$ [h$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(PPh$_3$)$_4$Ru(H)$_2$/tdppcy [10/11]</td>
<td>Al(OTf)$_2$ [2]</td>
<td>EtOH</td>
<td>107.8</td>
<td>7.40</td>
<td>8.79</td>
<td>218</td>
</tr>
<tr>
<td>3[c]</td>
<td>(PPh$_3$)$_4$Ru(H)$_2$/tdppcy [5/5.5]</td>
<td>Al(OTf)$_2$ [2]</td>
<td>THF</td>
<td>81.2</td>
<td>2.45</td>
<td>3.05</td>
<td>66</td>
</tr>
<tr>
<td>4[d]</td>
<td>(PPh$_3$)$_4$Ru(H)$_2$/tdppcy [5/5.5]</td>
<td>Al(OTf)$_2$ [1]</td>
<td>THF</td>
<td>85.1</td>
<td>2.45</td>
<td>4.58</td>
<td>83</td>
</tr>
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<td>5</td>
<td>(tdppcy)Ru(tmm) [5]</td>
<td>Al(OTf)$_2$ [1]</td>
<td>EtOH</td>
<td>72.3</td>
<td>7.80</td>
<td>6.80</td>
<td>458</td>
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<td>6</td>
<td>(tdppcy)Ru(tmm) [5]</td>
<td>Al(OTf)$_2$ [1]</td>
<td>THF</td>
<td>71.3</td>
<td>0.90</td>
<td>5.44</td>
<td>50</td>
</tr>
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<td>7</td>
<td>(triphos)Ru(tmm) [5]</td>
<td>Al(OTf)$_2$ [1]</td>
<td>THF</td>
<td>14.1</td>
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<td>0.90</td>
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<td>8</td>
<td>(triphos)Ru(tmm) [5]</td>
<td>Al(OTf)$_2$ [1]</td>
<td>EtOH</td>
<td>44.8</td>
<td>4.24</td>
<td>2.90</td>
<td>198</td>
</tr>
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</table>

[a] $V_{\text{solvent}} = 4$ mL, $p(H_2/CO_2)$ [bar/bar] = 90/30 at r.t., $T = 120$ °C, $t = 20$ h. [b] determined by $^1$H-NMR-spectroscopy with mesitylene as internal standard. [c] stirring speed = 1000 rpm. [d] stirring speed = 1500 rpm.
References


