N2 fixation and dehydrogenation of methanol and formic acid with late transition metal complexes

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Chapter 2

Reactivity of a ruthenium-carbonyl complex in the methanol dehydrogenation reaction

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Chapter 2

2.1 Introduction

The transformation to a society based on renewable energy requires both the harvesting of sustainable energy (wind and solar) as well as the transformation of this energy into proper energy carriers. In this context, the use of \( \text{H}_2 \) is an attractive energy carrier as it can be generated with sustainable energy by water-splitting, and it’s energy can be released by combustion or in a fuel cell providing water as only by-product.\(^1\) The storage of molecular hydrogen as a gas is challenging as it has low volumetric density.\(^5\) One possibility to overcome this limitation is to reversibly store \( \text{H}_2 \) in the form of a different chemical energy carrier. In this context methanol is an attractive hydrogen carrier; being a liquid at room temperature and containing a substantial amount (12.6%) of hydrogen.\(^6\) The use of methanol as a hydrogen storage carrier requires the development of catalysts that allow reversible dehydrogenation of methanol to \( \text{CO}_2 \) under mild reaction conditions. Dehydrogenation of methanol to carbon dioxide typically proceeds via the three steps depicted in Figure 1: The release of the first equivalent of \( \text{H}_2 \) results in the formation of formaldehyde, which when reacted with one equivalent of water releases the second equivalent of \( \text{H}_2 \) to yield formic acid. Finally, formic acid is dehydrogenated to form carbon dioxide, producing the third equivalent of \( \text{H}_2 \). Under basic conditions carbon dioxide is trapped in the form of carbonate, leading to a clean gas outlet of pure hydrogen.

![Figure 1: Proposed intermediates in the transition metal catalyzed methanol dehydrogenation reaction.](image)

The full dehydrogenation of methanol to \( \text{CO}_2 \) in presence of water has only been reported in 2013 by the groups of Beller\(^7\) and Grützmacher.\(^8\) Their systems consist of ruthenium catalysts capable of performing this reaction in aqueous media at temperatures below 100 °C. In the absence of base, Beller’s ruthenium-PNP system (Ru–PNP = RuHCl(CO) (PNP), PNP = HN(C\(\text{H}_4\)P(i-Pr))\(_2\)) reaches a turnover frequency (TOF) of almost 22 h\(^{-1}\) and Grützmacher’s ruthenium-trop\(_2\)dad system (Ru–trop\(_2\)dad = [K(dme)]\([\text{RuH(trop}_2\text{dad})]\)), trop\(_2\)dad = 1,4-bis(5H-dibenzo[a,d]cyclohepten-5-yl)-1,4-diazabuta-1,3-diene) a TOF of 54 h\(^{-1}\). The addition of KOH leads to an almost 30-fold increase of activity (TOF = 613 h\(^{-1}\)) for Beller’s system.\(^9\) Dehydrogenation of paraformaldehyde in the presence of water releasing two equivalents of hydrogen has also been reported by the group of Prechtl.\(^10\) Previously, our group reported new catalysts for the (reversible) dehydrogenation of formic acid.\(^11\) In search for new catalytic systems for the full dehydrogenation of
methanol we turned our attention to salen-type ligands. In this chapter we will report the use of ruthenium complexes based on salen ligands as catalyst for the methanol dehydrogenation reaction. Salen ligands can be easily prepared by a one-step condensation, which in principle gives facile access to high structural diversity. An active system could thus easily be tuned by changing e.g. the steric and electronic properties of the ligand.\textsuperscript{[15–17]} Notably, complexes of ruthenium and iron with Schiff base-derived ligands were already shown to activate alcohols in catalytic transfer hydrogenation reactions.\textsuperscript{[18–22]}

### 2.2 Results and Discussion

We aimed at the synthesis of a ruthenium complex with the “salbinapht” ligand (salbinapht = (R)-2′,2′-bis(salicylideneamino)-1,1′-binaphthyl, \(1\), Figure 2). This ligand features a binaphthyl backbone that enforces a \textit{cis-\(\beta\)} geometry around the metal. Such geometry enables two \textit{cis} vacant sites in the metal coordination sphere,\textsuperscript{[24,25]} which could facilitate an inner-sphere dehydrogenation process. Our initial attempts to synthesize a ruthenium complex with salbinapht ligand \(1\) revealed that when \(\text{Ru(Cl)}\text{(DMSO)}\text{_4}\) was reacted with \(1\) in methanol in the presence of LiOMe and triisopropylphosphine, complex \(2\) was formed in moderate yields: \(-20\%\) (Figure 2).

![Figure 2: The compounds discussed in this chapter. Complex 4 was previously reported by Werner et al.\textsuperscript{[23]}](#)

The proton and phosphorus NMR spectra of \(2\) confirm the presence of one triisopropylphosphine ligand coordinated to the ruthenium center. The aromatic region
in the ¹H-NMR spectrum of 2 shows the loss of symmetry of the salbinapht ligand, which indicates that the cis-β geometry is indeed adopted. Interestingly, only one imino-proton (7.1 ppm) could be identified in the ¹H NMR spectrum and new signals appeared in the region between 3.5 and 5.5 ppm that corresponds to a -CH₂NH- moiety. This suggests that one of the imine groups of ligand 1 has been hydrogenated during complex formation. IR spectroscopy reveals an intensive band at $\nu = 1919$ cm⁻¹ indicative for the presence of a CO-ligand. This carbonyl ligand must stem from methanol/methoxide used in the synthesis of the complex as no other CO-source was used. Thus, the spectroscopic analysis suggests that complex 2 is a 6-coordinate species containing one tetradentate dihydro-salbinapht, one triisopropylphosphine- and one carbonyl ligand. Recrystallization of complex 2 from acetonitrile gave yellow-orange crystals suitable for single crystal X-ray diffraction.

The crystal structure (Figure 3) is in accordance with spectroscopic analysis, and reveals the expected octahedral coordination environment around ruthenium. The 1-H ligand is coordinated in a cis-β fashion with one of the n-donating phenolato groups coordinated trans to the n-accepting carbonyl and the other trans to the imine. As a consequence, the σ-donating phosphine is coordinated trans to the σ-donating amine. To date only two examples of the regioselective monoreduction of a chiral salen ligand were reported. Complex 2 has three stereo centers (Ru, N, binaphthyl backbone). Remarkably, only one diastereoisomer of 2 is formed during the synthesis. The enantiopurity of complex 2 in the crystal structure in the non-centrosymmetric space group P1 has been confirmed using the Flack parameter (see experimental section, crystal data of 2).

Since complex 2 is coordinatively saturated, it was not obvious that it would catalyze the dehydrogenation of methanol. However, we anticipated that under basic conditions the carbonyl ligand could undergo the water gas shift reaction with the water present...
in the reaction mixture.\textsuperscript{[39–31]} Therefore, we investigated the activity of 2 as a catalyst in the methanol dehydrogenation reaction (Table 1). Dioxane was used as a co-solvent during the catalytic reaction since complex 2 has low solubility in methanol/water. Hydrogen evolution was measured volumetrically. Samples of the evolved gas were analyzed using gas chromatography. Molecular hydrogen was always the only gas formed and no CO could be detected. In the 8 M KOH solution experiment, complex 2 showed moderate activity (TOF = 55 h\textsuperscript{-1}, Table 1, entry 1). The decrease of the amount of base led to lower reaction rates, which can (partially) be explained by the effect of the lower internal reaction temperature (resulting from a lower boiling point of the reaction mixture, entries 2 and 3). Analysis of the reaction mixture of entry 1 after extraction with dichloromethane and using NMR spectroscopy reveals the presence of both formate (HCOO\textsuperscript{-}) and carbonate (CO\textsubscript{3}\textsuperscript{2-}) salts (see experimental section, \textsuperscript{1}H- and \textsuperscript{13}C-NMR of reaction mixture after catalysis). The presence of these salts shows that water is involved in the overall dehydrogenation reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Concentration base</th>
<th>(T_{\text{in}}) \textsuperscript{(b)} (°C)</th>
<th>TOF (h\textsuperscript{-1})</th>
</tr>
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<tr>
<td>1</td>
<td>KOH</td>
<td>8 M</td>
<td>82</td>
<td>55</td>
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<td>2</td>
<td>KOH</td>
<td>6 M</td>
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<td>37</td>
</tr>
<tr>
<td>3</td>
<td>KOH</td>
<td>4 M</td>
<td>76</td>
<td>29</td>
</tr>
</tbody>
</table>

Table 1: Hydrogen generation from methanol with complex 2\textsuperscript{[a]}

\textsuperscript{[a]} Reaction conditions: 30 mL of solvent (25% dioxane, 75 % methanol/water (9:1) v/v), \~12 µmol of catalyst, base as described, reaction time of 4.5 hours, all experiments were measured in duplo. The oil bath was set to 110 °C to ensure reflux conditions for all measurements. \textsuperscript{[b]} Internal temperature of the refluxing solution.

Next, we investigated the mechanism of the methanol dehydrogenation reaction by our system. We first studied the source of both the hydrogen atoms on the hydrogenated imine and of the source of the carbonyl ligand. As the formation of the complex proceeds in absence of carbon monoxide, the carbonyl ligand must have been formed \textit{in-situ}. Therefore, we conducted isotope-labeling experiments using CD\textsubscript{3}OD or \textsuperscript{13}CH\textsubscript{3}OH for the synthesis of the corresponding 2-D\textsubscript{2} or 2-\textsuperscript{13}CO respectively. The \textsuperscript{1}H-NMR spectrum of the complex 2-D\textsubscript{2}, synthesized from CD\textsubscript{3}OD, revealed the absence of the peaks at 4.60 and 5.34 ppm due to the presence of deuterons at the reduced imine position. The use of \textsuperscript{13}CH\textsubscript{3}OH for the synthesis of 2-\textsuperscript{13}CO, confirmed that the carbonyl ligand is derived from methanol: the carbonyl signal in the \textsuperscript{13}C-NMR (205.30 ppm, d (\(^2J\textsuperscript{(3P-\textsuperscript{13}C)}) = 16.9 \text{ Hz}) was the only signal found in this region and the \textsuperscript{31}P NMR spectrum revealed a doublet at 60.43 ppm due to coupling with the \textsuperscript{13}CO (\(^2J\textsuperscript{(3P-\textsuperscript{13}C)}) = 17.7 \text{ Hz}). These labeling experiments confirm that methanol is the source of both the amine protons and the carbonyl ligand in complex 2.
Secondly, we performed the synthesis of 2 in a stepwise manner. As formation of ruthenium hydrido carbonyl complexes derived from alcohols in presence of phosphine ligands are well established reactions\cite{9,25,32,33}, it seemed possible that the dehydrogenation of methanol occurred first, followed by coordination of 1. To test this hypothesis, we first pre-formed the putative Ru(CO)$_2$(H)$_2$(P(i-Pr)$_3$)$_2$ (4) species (Figure 2),\cite{25} and subsequently added the salbinapht ligand 1. This modified procedure yielded 2 in much higher yields (80%) suggesting a mechanism in which the in-situ formed species 4 indeed reacts with the salbinapht ligand 1 to form 2. Thus, the methanol dehydrogenation reaction occurs first, in presence of ruthenium-phosphine species, after which coordination to ligand 1 leads to complex 2 as a single diastereoisomer.

![Figure 4: Investigation of the role of the CO-ligand.](image)

*observed by $^{13}$C-NMR
**typical gas evolution experiment similar to Table 1, entry 1

Subsequently we examined whether the carbonyl ligand is an intermediate in the methanol dehydrogenation reaction. The first experiment was conducted with regard to the extrusion of the CO-ligand from 2 to create a vacant site for methanol coordination. We anticipated that the water gas shift reaction (WGSR) may play a role in this process and therefore studied the effect of the base present in the reaction mixture. An NMR experiment was conducted in which the $^{13}$CO-labelled complex 2 was reacted with base in a high-pressure NMR tube at elevated temperatures (Figure 4, experiment 1). For this experiment, we used the same reactant ratios as used during the catalysis experiment in Table 1 (entry 1), but in a high-pressure NMR tube. Heating 2-$^{13}$CO in a KOH solution of MeOH, H$_2$O and THF at 100 °C resulted in the total disappearance of the ruthenium carbonyl signal within 3.5 hours (see experimental section, investigation of the role
of the CO-ligand, experiment 1). Dissolution of the white precipitate in D$_2$O showed the presence of $^{13}$C-enriched potassium formate (as evidenced by $^1$H and $^{13}$C NMR). Injection of the headspace showed presence of molecular hydrogen (as evidenced by gas chromatography). From this data, we conclude that the CO-ligand that is obtained from methanol (as was evidenced earlier by the formation of $^{2-13}$CO from $^{13}$CH$_3$OH), can be further reacted with base, forming potassium formate. Importantly, several current homogeneous methanol dehydrogenation catalysts feature “spectator” CO-ligands.[7,34–37]

In view of the above results it is plausible that under catalytic conditions these catalysts can lose CO through nucleophilic attack of base present in the reaction mixture to create a new vacant site. This extra vacant site could also play a role in the overall mechanism for these catalysts.

In a subsequent experiment, we explored if complex 2 can be regenerated from methanol during catalysis after it has been attacked by base. Therefore, we applied standard reaction conditions similar to entry 1 (8M KOH, 25% dioxane, 75% methanol-water (9:1) 12 µmol of catalyst at reflux temperature) but this time in the presence of 50% labeled $^{13}$CD$_3$OD (Figure 2.4, experiment 2). After 2 hours, the still active reaction mixture was extracted with dichloromethane and its $^{13}$C-NMR spectrum was measured. No $^{13}$C-enriched ruthenium-carbonyl signal corresponding to $^{2-13}$CO could be detected. The water phase, however, did show the presence of H/D$^{13}$COO$^-$ when measured in D$_2$O as became evident from $^{13}$C-NMR and $^1$H-NMR spectroscopy (see experimental section, investigation of the role of the CO-ligand, experiment 2). The presence of formate indicates that the $^{13}$C-labelled methanol is dehydrogenated over the course of 2h, and that the resting state of the actual catalyst does not contain a carbonyl ligand. The $^1$H-NMR spectrum did reveal the presence of salen-derived species with a different $^1$H-NMR spectrum than that of ligand 1 or complex 2. Unfortunately, we were unable to determine the complete structure of these salen species as it was not possible to isolate the compound in pure form from the complex reaction mixture. The above described experiments show that the carbonyl ligand of complex 2 can be extruded under basic conditions used during catalysis. The formation of the labeled catalyst ($^{2-13}$CO) and subsequent isolation of the labeled formate (H$^{13}$COO$^-$) after reaction with base shows two steps of the methanol dehydrogenation with ruthenium. The fact that the labeled complex $^{2-13}$CO is not regenerated from $^{13}$CH$_3$OH during catalysis shows that complex 2 is not the resting state during catalysis. Probably other unidentified salen-derived species are formed that lack a CO-ligand, which could not be isolated.

Traces of complex 4 were occasionally found after catalytic reactions and (since complex 2 is prepared from complex 4) its performance in the dehydrogenation reaction was investigated. The activity of complex 4 was studied under conditions similar to the experiment described in Table 2.1, entry 1 (see experimental section, Catalytic experiments with catalyst), and revealed similar activity (TOF = 50 h$^{-1}$) as found for the reaction with
complex 2. Thus, it is possible that the \textit{in situ} formed 4 is at least partially responsible for methanol dehydrogenation during catalysis. The above result leaves the question whether the active species generated from 2 is still coordinated to a salbinapht ligand. Therefore, we investigated the activity of Ru(1)(DMSO)$_2$ (3) (an analogue of 2, Figure 2), which does not feature a phosphine nor a carbonyl ligand, in the methanol dehydrogenation reaction. Complex 3, subjected to catalytic conditions (similar to Entry 1, Table 1), shows hydrogen evolution in the first 30 minutes (TON$_{30\text{min}}$ = 23), as determined volumetrically and analyzed by gas GC (see experimental section, catalytic experiments with catalyst). This suggests that a ruthenium center supported with a salbinapht ligand (1) is capable of catalyzing the dehydrogenation of methanol. However, under the applied conditions the catalyst has low stability and the presence of a coordinated phosphine ligand clearly has a beneficial influence on the overall performance of complex 2.

2.3 Conclusions

In conclusion, we have demonstrated that salen based ruthenium complexes can be used as catalysts for the methanol dehydrogenation reaction. The ruthenium complex based on salen ligand 1 is capable of transforming methanol into molecular hydrogen, formate and carbonate. Mechanistic investigations demonstrate that the CO on the carbonyl ruthenium complex can be attacked by a base (such as MeO$^-$ or OH$^-$) to form formate and carbonate. The carbonyl complex is, however, not the resting state of the catalytic reaction. Future experiments should focus on the design of more active and stable catalysts systems, which may be achieved by moving to complexes based on phosphino-Schiff bases, which also are already being used for transfer hydrogenation reactions. Initial experiments with such ruthenium complexes show that they can indeed dehydrogenate methanol to form molecular hydrogen.

2.4 Experimental section

General methods

All reactions were carried out under an inert (argon/nitrogen) atmosphere using standard Schlenk techniques. THF was distilled from sodium benzophenone ketyl; acetonitrile, methanol and dichloromethane were distilled from CaH$_2$ and dioxane was distilled from sodium all under nitrogen. NMR spectra (H, $^{13}$C and $^{31}$P, H-H COSY and HSQC) were measured on a Bruker AMX 400, a Varian Mercury 300, a Bruker DRX 500, or a Bruker DRX 300 spectrometer. Infrared spectra were recorded on a Thermo Nicolet NEXUS 670
FT-IR. The high-resolution mass spectra were recorded on a JEOL AccuTOF LC, JMS-T100LP mass spectrometer using electron spray ionization (ESI) on a JEOL AccuTOF GC v 4g, JMS-T100GCV mass spectrometer using field desorption (FD).

**Synthesis of compounds**

(R)-2,2'-bis(salicylideneamino)-1,1'-binaphthyl (1): a solution of 1.05 g of (R)-1,1-binaphthyl-2,2'-diamine (3.67 mmol) in ethanol (25 mL) was transferred to a 100 mL flame dried Schlenk flask equipped with a reflux condenser. To this chalky brown suspension 0.80 mL of the salicylaldehyde (7.51 mmol) dissolved in 30 mL ethanol was added drop wise and heated under reflux for 2h. The reaction mixture was cooled to room temperature and concentrated to 4-5 mL. The precipitated yellow product was then filtered off and washed with ethanol (1 x 5 mL) and pentane (2 x 5 mL) and dried to give ligand 1 in pure form (1.71 g, 94 %). Spectra were in agreement with literature.[38,39] 

^1H-NMR (500 MHz, DMSO-d$_6$): δ 12.24 (s, 2H), 9.08 (s, 2H), 8.32 – 8.18 (m, 2H), 8.08 (d, J = 8.1 Hz, 2H), 8.00 (d, J = 9.0 Hz, 2H), 7.48 (d, J = 7.9 Hz, 4H), 7.31 (s, 2H), 7.23 (s, 2H), 7.05 (d, J = 8.5 Hz, 2H), 6.83 (s, 2H), 6.61 (d, J = 8.2 Hz, 2H). ^13C-NMR (126 MHz, DMSO d$_6$): δ 162.73, 160.03, 142.90, 133.10, 132.71, 132.60, 132.25, 129.89, 129.56, 128.38, 127.11, 125.97, 125.67, 119.08, 118.87, 117.15, 116.40, 40.11, 40.02, 39.94, 39.86, 39.78, 39.69, 39.61, 39.52, 39.44, 39.35, 39.19, 39.02.

Ru(1-H$_2$)(CO)P(i-Pr)$_3$·MeCN (2): 100 mg (0.21 mmol) of Ru(Cl)$_2$(DMSO)$_4$ was transferred to a flame dried Schlenk flask equipped with a reflux condenser and the vessel was purged three times with argon-vacuum cycles. Then 10 mL of methanol was added, followed by the addition of 80 µL (0.42 mmol) of P(i-Pr)$_3$. The colorless solution with suspended yellow solid was heated under reflux until the solid had dissolved and the solution turned orange-red (approximately 5 minutes). The reaction mixture was cooled to room temperature after which 0.42 mL of a LiOMe solution (0.42 mmol, 1M in methanol) was added and stirred for 5 minutes. Then the orange solution was brought to reflux for 30 minutes. In the meantime, 102 mg (0.21 mmol) of (R)-2,2'-bis(salicylideneamino)-1,1'-binaphthyl (1) was transferred to a different flame dried Schlenk flask, which was purged three times with argon-vacuum cycles. To this yellow solid 20 mL of methanol and 0.42 mL (2.55 mmol) of LiOMe-solution (1M in methanol) where added. The yellow suspension was added via a syringe to the stirring solution containing the ruthenium phosphine complex. The reaction mixture was heated for 45 min which resulted the formation of an orange solution. The reaction mixture was concentrated in vacuo to approximately 2 mL, leading to the formation of an orange-yellow precipitate. The filtrate was removed using a syringe.
and the orange-yellow solid was dried and subsequently recrystallized from acetonitrile giving the orange-yellow crystalline complex in pure form. The acetonitrile filtrate was concentrated to ~1 mL giving a second crop of 2. Overall yield: 148 mg, 90 %. Only one diastereoisomer is formed during the synthesis: the N-atom of the amine group (N-H) has S configuration, the ruthenium center is coordinated in a OC-6-56-A configuration, and binaphthyl remains in R configuration.

$^1$H-NMR (500 MHz, CD$_3$CN): δ 8.12 (d, $J = 8.7$ Hz, 1H), 8.02 (d, $J = 8.3$ Hz, 1H), 7.70 (d, $J = 8.3$ Hz, 1H), 7.68 – 7.62 (m, 2H), 7.60 (d, $J = 8.7$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.7$ Hz, 1H), 7.33 (t, $J = 7.4$ Hz, 1H), 7.22 (d, $J = 8.6$ Hz, 1H), 7.16 (t, $J = 7.8$ Hz, 1H), 7.10 (s, 1H), 7.05 (t, $J = 8.7$, 6.9, 1.8 Hz, 1H), 7.00 (d, $J = 7.2$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.76 (d, $J = 8.6$ Hz, 1H), 6.66 (d, $J = 8.6$ Hz, 1H), 6.55 (d, $J = 8.1$ Hz, 1H), 6.39 (t, $J = 7.3$ Hz, 1H), 6.20 (d, $J = 7.7$ Hz, 1H), 6.06 (t, $J = 7.3$ Hz, 1H), 5.47 – 5.23 (m, 1H), 4.60 (t, $J = 10.5$ Hz, 1H), 3.76 – 3.62 (m, 1H), 2.73 – 2.46 (m, 3H), 1.26 (ddd, $J = 123.5$, 13.2, 7.2 Hz, 18H).

$^{31}$P-NMR (202 MHz, CD$_3$CN): δ = 60.44. $^{13}$C-NMR (126 MHz, (CD$_3$)$_2$SO): δ 204.21, 162.73, 160.03, 142.90, 133.10, 132.71, 132.60, 132.25, 129.89, 129.56, 128.38, 127.11, 125.97, 125.67, 119.08, 118.87, 117.15, 116.40, 40.11, 40.02, 39.94, 39.86, 39.78, 39.69, 39.61, 39.52, 39.44, 39.35, 39.19, 39.02. ν$_{CO}$ = 1919 cm$^{-1}$. Mass Analysis (ESI) [2-H]: calc: 783.2302. found: 783.2360.

Ru(1-H$_2$)$^{(13}$CO)P(i-Pr)$_3$· MeCN (2-$^{13}$CO): 78.5 mg (0.16 mmol) of Ru(Cl)$_2$(DMSO)$_4$ was transferred to a flame dried Schlenk flask equipped with a reflux condenser and the vessel was purged three times with argon-vacuum cycles. Then 3 mL of $^{13}$C-labelled methanol was added, followed by the addition of 0.11 mL (0.56 mmol) of P(i-Pr)$_3$. The colorless solution with suspended yellow solids was heated under reflux until the solid had dissolved and the solution turned orange-red (approximately 5 minutes). In the meantime, 81.1 mg (0.16 mmol) of the (R)-2,2’-bis(salicylideneamino)-1,1’-binaphthyl (1) was transferred to a different flame dried Schlenk flask, which was purged three times with argon-vacuum cycles. To this yellow solid, 3 mL of $^{13}$C-labelled methanol and 8 mg (0.35 mmol) of solid sodium where added. The resulting yellow suspension was added via a syringe to the stirring solution containing the ruthenium phosphine complex. The reaction mixture was heated for 55 min which resulted in a dark red solution that gave an orange-yellow precipitate upon concentration of the solvent to ±1 mL. After standing one day at 5 °C, the filtrate was taken off and the orange-yellow solid was dried and subsequently recrystallized from 2 mL hot acetonitrile, giving the orange-yellow crystalline complex in pure form. The acetonitrile filtrate was cooled in the freezer at -20 °C giving a second crop of 2-$^{13}$CO. Overall yield: 65.7 mg, 51 %. $^1$H-NMR (300 MHz, CD$_3$CN): δ 8.12 (d, $J = 8.8$ Hz, 1H), 8.02 (d, $J = 8.2$ Hz, 1H), 7.77 – 7.56 (m, 4H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.44 – 7.28 (m, 2H), 7.29 – 7.13 (m, 2H), 7.13 – 6.87 (m, 4H), 6.76 (d, $J = 8.6$ Hz, 1H), 6.66
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(d, J = 8.6 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 6.39 (t, J = 7.3 Hz, 1H), 6.20 (d, J = 7.9, 1.9 Hz, 1H), 6.06 (t, J = 7.3 Hz, 1H), 5.40 – 5.27 (m, 1H), 4.60 (t, J = 10.4 Hz, 1H), 3.80 – 3.60 (m, 1H), 2.76 – 2.39 (m, 3H), 1.38 (dd, J = 13.7, 7.2 Hz, 1H), 1.14 (dd, J = 12.5, 7.2 Hz, 9H). 31P-NMR (122 MHz, CD3CN): δ 60.43 (d, J = 17.7 Hz).

13C-NMR-13CO (75 MHz, CD3CN): δ 205.30 (d, J = 16.9 Hz).

Ru(1-D2)(CO)P(i-Pr)3·MeCN (2-D2): Complex 2-D2 was prepared using the same procedure as for 2-13CO, using CD3OD instead of 13CH3OH. 1H-NMR (300 MHz, CD3CN): δ 8.12 (d, J = 8.8 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.77 – 7.56 (m, 4H), 7.52 (t, J = 7.6 Hz, 1H), 7.44 – 7.28 (m, 2H), 7.29 – 7.13 (m, 2H), 7.13 – 6.87 (m, 4H), 6.76 (d, J = 8.6 Hz, 1H), 6.66 (d, J = 8.6 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 6.39 (t, J = 7.3 Hz, 1H), 6.20 (d, J = 7.9, 1.9 Hz, 1H), 6.06 (t, J = 7.3 Hz, 1H), 3.80 – 3.60 (m, 1H), 2.76 – 2.39 (m, 3H), 1.38 (dd, J = 13.7, 7.2 Hz, 1H), 1.14 (dd, J = 12.5, 7.2 Hz, 9H). 31P-NMR (122 MHz, CD3CN): δ 60.44.

[Ru(1-H)(CO)P(i-Pr)3]K·1.5THF: 18.3 mg (0.023 mmol) of 2 was added to a flame dried Schlenk and purged 3x with vacuum argon cycles. 1 mL of THF followed by 0.023 mL (0.023 mmol) of tBuOK (1 M in THF) was added resulting in an immediate color change from orange to deep red. After stirring for 5 minutes the solvent was evaporated. Although the sample was dried for 3 days under vacuum, THF present in the sample. The THF peak partly overlaps with one of the CH2 protons. In solution, 2a spontaneously oxidizes to the double imine 2aa within one day, which precluded the measurement of 13C-NMR. 1H-NMR (500 MHz, (CD3)2SO) (2a): δ 7.85 (t, J = 9.0 Hz, 2H), 7.47 – 7.21 (m, 6H), 7.13 (t, J = 7.7 Hz, 1H), 6.98 (d, J = 8.5 Hz, 1H), 6.83 (t, 2H), 6.74 – 6.64 (m, 3H), 6.44 (d, J = 7.8 Hz, 1H), 6.37 (d, J = 8.6 Hz, 1H), 6.30 (d, J = 7.9 Hz, 1H), 6.26 – 6.04 (m, 2H), 5.93 (t, J = 7.2 Hz, 1H), 4.17 (d, J = 11.1 Hz, 1H), 3.58 (d, 1H), 2.58 – 2.44 (m, 3H), 1.23 (ddd, 18H).

31P-NMR (202 MHz, D(CD3)2SO): δ 47.93 (s).

Ru(1)(DMSO)2 (3): 103.4 mg (0.21 mmol) of (R)-2,2'-bis(salicylideneamino)-1,1'-binaphthyl (1) and 95.4 mg (3.98 mmol) of NaH were transferred to a Schlenk flask and purged 3x with vacuum argon cycles. Then 4.5 mL of THF was added and this suspension was stirred until gas evolution had ceased. The yellow solution was filtered off, the white solid was washed with 3x 2mL THF and the combined filtrates were evaporated to dryness. To this yellow solid was added 64.9 mg (0.11 mmol)
of [Ru(Cl)$_2$-$p$-cymene]$_2$ which was purged 3x with vacuum argon cycles. Then 10 mL of MeCN was added and the solution was stirred overnight. The resulting orange suspension was filtered and the solids were washed with DCM. The filtrates were combined and evaporated to dryness resulting in an orange red solid. This solid was dissolved in 3 mL DMSO and stirred overnight. After evaporation of the DMSO and $p$-cymene, the product was obtained in pure form. Yield: 159.3 mg, 99%

$^1$H-NMR (300 MHz, CD$_3$OD) δ 8.47 (s, 1H), 8.02 (dd, $J = 8.5, 4.7$ Hz, 2H), 7.75 (dd, $J = 8.4, 5.4$ Hz, 2H), 7.64 (s, 1H), 7.61 (d, 1H), 7.48 (t, $J = 8.1, 6.7, 1.4$ Hz, 1H), 7.40 – 7.02 (m, 6H), 6.91 (d, $J = 8.6$ Hz, 1H), 6.76 (dd, $J = 8.6, 4.5$ Hz, 2H), 6.66 (d, $J = 8.0, 1.8$ Hz, 1H), 6.54 (t, $J = 7.4$ Hz, 1H), 6.27 (t, $J = 7.4$ Hz, 1H), 3.06 (s, 3H), 3.03 (s, 3H), 2.64 (s, 3H), 1.43 (s, 3H).

**Synthesis of Ru(CO)$_2$(H)$_2$($i$-Pr)$_3$$_2$(4):**

102.5 mg (0.214 mmol) of Ru(Cl)$_2$(DMSO)$_4$ was added to a flame dried Schlenk and purged 3x with vacuum argon cycles. Then 10 mL of methanol and 83 µL (0.427 mmol) of P($i$-Pr)$_3$ were added and this was heated to reflux for 1h turning into a red solution. The solution was cooled to room temperature, 0.85 mL of LiOMe (1M, 0.85 mmol) was added and stirred for 5 minutes after which the solution was heated to reflux and stirred overnight yielding an orange/brown solution. The solution was filtered and evaporated to dryness in vacuo. The solid was extracted with dichloromethane and the yellow product was crashed out adding pentane to this solution giving a yellow solid that matched literature data[25]. The solid was used without further purification for catalysis.

**Hydrogen evolution experiments**

In a typical gas evolution experiment the specified amount of base was transferred to a flame dried setup as depicted on the right and purged 3x with vacuum argon cycles until point “A”. Then 29 mL of solvent (20.3 mL of methanol, 2.2 mL of water and 6.5 mL of dioxane) was added and the mixture was heated to reflux, while flushing the tube and the cylinder until point “B” with argon. When reflux temperature was reached, the flushing was ended and heating was continued for 0.5-1 h. Meanwhile, ~12-13 µmol of the specified ruthenium complex was transferred to another flame dried Schlenk flask, purged 3x with...
vacuum argon cycles and subsequently dissolved in a total amount of 1.5 mL dioxane. This catalyst solution was added to the refluxing mixture and the measurement of gas evolution was started. The displacement of water in the cylinder was measured in time (Figure 5 and Figure 6). All catalysis runs were measured in duplo and the gas formed was injected in the gas GC after every measurement. Molecular hydrogen was always the only gas present. TON were calculated using equation 1. $^1$H-NMR and $^{13}$C-NMR of the reaction mixture showed formation of potassium formate and carbonate (Figure 7 and Figure 8).

Figure 5: Hydrogen evolution with complex 2 as detected volumetrically using three different concentrations of KOH (8M KOH: squares; 6M KOH: dots; 4M KOH: triangles).

Figure 6: Hydrogen evolution using complex 2 (triangle), complex 3 (dot) and complex 4 (square) using conditions similar to Table 2.1, entry 1.

Figure 7: $^1$H-NMR spectrum (D$_2$O) of solid after hydrogen production showing the formate (8.54 ppm) (black line); with additional formate added to the NMR tube (grey line).

Figure 8: $^{13}$C-NMR spectrum (D$_2$O) of solid after hydrogen production (Table 1, entry 1) showing the formate (170 ppm) and the carbonate (168 ppm) signals.
Calculation of TON

TON is calculated using equation 1:

\[ TON = \frac{V_{\text{obs}}}{V_m \cdot n_{\text{cat}}} \]  

(2.1)

\( V_{\text{obs}} \): measured gas volume displacement cylinder [mL]

\( V_m \): molar gas volume: 24.49 [mL/mmol]

\( n_{\text{cat}} \): amount of catalyst [mmol]

Investigation of the role of the CO-ligand

Experiment 1: Reaction of \(^{2-13}\)CO with methanol, KOH and \(H_2O\). 11.1 mg (0.014 mmol) of \(^{2-13}\)CO was transferred to an oven dried HP NMR tube and purged 4x with vacuum argon cycles. 0.1 mL of a premade 8M KOH solution in methanol/water (9/1 v/v) followed by 0.4 mL of THF-\(d_4\) was added. The solution was heated inside the NMR spectrometer at 100 °C, and the disappearance of the \(^{13}\)CO peak was followed in time (Figure 9). A sample of
the gas headspace was injected in the Gas GC, showing only molecular hydrogen to be present. Dissolution of the precipitated white solid in $D_2O$ showed presence of $^{13}C$-labelled formate in both H-NMR (8.25 ppm; the peak shift is effected by the amount of base present in solution) and $^{13}C$-NMR (171 ppm).

**Experiment 2**: Attempt to exchange $^{12}CO$ for $^{13}CO$ with $^{13}CD_3OH$ under standard catalytic conditions. A typical gas evolution experiment was set up using 13.50 mg of 2, in an 8M KOH solution of 8 mL dioxane, 9 mL CD$_3$OD, 11 mL $^{13}CD_3$OD and 2.2 mL water. Catalysis was ran for 2h producing molecular hydrogen in a linear way (Figure 10). The reaction mixture was cooled to room temperature and extracted with 1 x 10 mL and 1 x 5 mL of dichloromethane. The organic solution was evaporated to dryness and dissolved in MeCN-$d_3$; no enriched $^{13}CO$-signal could be detected in $^{13}C$-NMR. $^{13}C$-NMR of the methanol/water phase (Figure 11) showed presence of the $^{13}C$-enriched H/DCOO$^-$ indicating that the $^{13}C$-labelled methanol was dehydrogenated. Thus, the carbonyl complex is not regenerated after the attack of base on the carbonyl.

**Figure 10**: Hydrogen evolution from methanol while attempting to exchange 2 for $^{13}CO$ with $^{13}CD_3OH$.

**Figure 11**: APT-spectrum of the reaction mixture.

### X-ray crystal structure determination of 2⋅2CH$_3$CN

$C_{44}H_{44}N_{4}O_{3}PRu\cdot2CH_3CN$, Fw = 863.96, yellow-orange block, 0.28 x 0.23 x 0.16 mm$^3$, triclinic, P1 (no. 1), a = 11.7197(5), b = 11.7886(5), c = 16.9812(9) Å, $\alpha = 103.014(2)$, $\beta = 90.074(1)$, $\gamma = 111.683(2)$°, $V = 2114.84(16)$ Å$^3$, $Z = 2$, $D_g = 1.357$ g/cm$^3$, $\mu = 0.46$ mm$^{-1}$. The crystal appeared to consist of three fragments. The first and second fragment are related by a twin relation with a twofold rotation about $uvw$=[0,0,1] as twin operation. The third fragment has an arbitrary orientation of 3.9° with respect to the second fragment. Because of this crystal splitting, three orientation matrices were used for the integration with the Eval 15 software.$^{[41]}$ 51792 Reflections were measured on a Bruker Kappa Apex II diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.65$ Å$^{-1}$. Multiscan absorption correction and scaling was performed with TWINABS$^{[42]}$ (correction range 0.72-0.75). 20002 Reflections were unique ($R_{int} = 0.026$), of which 19336 were observed [I>2$\sigma$(I)]. The structure was solved with Patterson overlay methods using SHELXT.$^{[43]}$ Least-squares refinement was performed with SHELXL2013.$^{[44]}$
against \( F^2 \) of all reflections using a HKLF-5 reflection file\(^{[46]} \). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. N-H hydrogen atoms were located in difference Fourier maps and were refined freely with isotropic displacement parameters. All other hydrogen atoms were introduced in calculated positions and refined with a riding model. 1053 Parameters were refined with 3 restraints (floating origin). \( R_1/ \text{wrR}_2 [\text{I} > 2\sigma(\text{I})] \): 0.0225 / 0.0560, \( R_1/\text{wrR}_2 [\text{all refl.}] \): 0.0239 / 0.0566, \( S = 1.027 \). Batch scale factors of the second and third crystal fragment \( \text{BASF} = 0.3085(8)/0.1082(7) \). The Flack parameters\(^{[46]} \) were determined by refining the structure against the non-overlapping reflections of the three fragments, resulting in \( x = -0.004(6), -0.020(9), \) and \(-0.012(16)\) for the three fragments, respectively. Residual electron density between 0.44 and 0.49 e/Å\(^3\). Geometry calculations and checking for higher symmetry were performed with the PLATON program\(^{[47]} \). CCDC 1477274 contains the supplementary crystallographic data for this paper. These

\[\text{Figure 11: Ortep drawing of } 2 \text{ (50 % probability ellipsoids). The second independent molecule, four acetonitrile molecules and most hydrogen atoms are omitted for clarity.'}\]

\[\text{Figure 12: Quaternion fit of the two independent molecules in } 2 \text{. The two molecules are approximately related by a non-crystallographic twofold rotation about } uvw=[0,0,1]. \text{ This relation corresponds to the twin relation present in the crystal.}\]

\[\text{Selected bond lengths [Å] and angles [°]: Ru1-P1 2.3431(9); Ru1-O11 2.069(2); Ru1-O21 2.088(2); Ru1-N11 2.063(3); Ru1-N21 2.285(3); Ru1-C441 1.825(4); Ru2-P2 2.3452(9); Ru2-O12 2.074(2); Ru2-O22 2.081(3); Ru2-N12 2.056(3); Ru2-N22 2.292(3) Ru2-C442 1.821(4); P1-Ru1-O11 92.35(8); P1-Ru1-O21 85.36(8); P1-Ru1-N11 100.95(9); P1-Ru1-N21 173.99(8); P1-Ru1-C441 91.30(11); O11-Ru1-O21 83.60(10); O11-Ru1-N11 88.14(10); O11-Ru1-N21 83.57(11); O11-Ru1-C441 175.23(14); O21-Ru1-N11 169.82(11); O21-Ru1-N21 89.79(10); O21-Ru1-C441 93.64(13); N11-Ru1-N21 83.37(11); N11-Ru1-C441 94.18(14); N21-Ru1-C441 92.55(14); N12-Ru2-C442 93.69(13); N22-Ru2-C442 92.79(14); O12-Ru2-O22 83.77(10); O12-Ru2-N12 88.06(11); P2-Ru2-O12 92.84(8); P2-Ru2-O22 84.95(8); P2-Ru2-N12 100.92(9); P2-Ru2-N22 173.64(8); P2-Ru2-C442 91.06(11); N12-Ru2-N22 83.89(11); O22-Ru2-N12 170.18(11); O12-Ru2-N22 83.10(11); O12-Ru2-C442 175.35(14); O22-Ru2-N22 89.72(11); O22-Ru2-C442 94.07(13).}\]

data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
2.5 References

Chapter 2