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Methanol as Hydrogen Source: Transfer Hydrogenation of Aldehydes near Room Temperature

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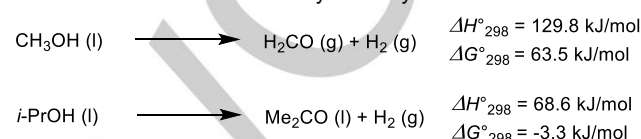   Liverpool, L69 7ZD (UK)
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Abstract: A cyclometalated rhodium complex has been found to show excellent activity in dehydrogenation of methanol at room temperature. This feature allows for the catalytic transfer hydrogenation of various aldehydes with methanol as both hydrogen source and solvent under very mild conditions. A hydroxy functionality on the ligand is shown to be critical for this unusual activity.

Reduction of carbonyl compounds is an essential synthetic method for obtaining valuable alcohol products in both academia and industry.[1] Transfer hydrogenation (TH) has attracted a great deal of attention in this area due to its simplicity, safety and low cost.[2] Compared with common hydrogenation, easily accessible hydrogen sources are used in TH instead of hazardous H_2. Conventionally, isopropanol and formic acid are used as the hydrogen donor in TH.[2,3] In contrast, the simplest, cheapest alcohol, methanol, has been much less employed in TH, although it could serve as an excellent hydrogen source in catalytic reactions.

Methanol is a promising hydrogen source and could be the base for a future economy, owing to its high hydrogen storage capacity of 12.5% (wt).[4] Methanol, easily derived from oil, coal and biomass, is one of the cheapest, most easily available and most easy-to-handle chemicals.[5] However, as a primary alcohol, methanol is generally considered thermodynamically unfavourable for the generation of H_2 or metal hydrides *via* dehydrogenation (Scheme 1),[6] although low-temperature dehydrogenation of methanol has recently been reported.[7] Dehydrogenation of isopropanol to acetone is considerably more favourable than that of methanol to formaldehyde, and thus the latter requires a higher energy input.[8] To date, only a few reports have appeared that describe the use of methanol as hydrogen source in catalytic TH; however, none of the thermal catalytic reactions could be performed around room temperature.[9-13] Thus, the Maitlis group early reported catalytic reduction of ketone by ruthenium and rhodium complexes with methanol at 150 °C.[9] Chen and co-workers demonstrated the selective TH of biomass-based furfural and 5-hydroxymethylfurfural with methanol on a copper catalyst at over 200 °C,[10] and the García group reported Ni-catalyzed alkylation and TH of α,β-unsaturated enones with methanol at 180 °C.[11] Using an iridium N-heterocyclic carbene complex in the presence of 5 equivalents of a base, the Crabtree group demonstrated TH of aromatic ketones and imines with methanol at 120 ºC.[12] More recently, Li and co-workers accomplished a much lower-temperature TH of ketones with methanol catalyzed by an iridium-bipyridonate complex, which proceeded at 66 °C.[13] As far as we are aware, there appear to be only two examples of room temperature TH reactions with

methanol. In one example, the TH is driven by light, while in the other the reaction is enabled by an enzyme.[14,7e]

$$CH_3OH\ (l) \longrightarrow H_2CO\ (g) + H_2\ (g) \qquad \begin{array}{l} \Delta H°_{298} = 129.8\ \text{kJ/mol} \\ \Delta G°_{298} = 63.5\ \text{kJ/mol} \end{array}$$

$$i\text{-PrOH}\ (l) \longrightarrow Me_2CO\ (l) + H_2\ (g) \qquad \begin{array}{l} \Delta H°_{298} = 68.6\ \text{kJ/mol} \\ \Delta G°_{298} = -3.3\ \text{kJ/mol} \end{array}$$

Scheme 1. Selected thermodynamic data for alcohol dehydrogenation.

As indicated by the thermodynamics and literature, low-temperature TH with methanol is challenging. If the substrates are ketones or aldehydes, the challenge can be more significant, as the product, a secondary or primary alcohol, is expected to be dehydrogenated more easily than methanol. In our continued study of TH reactions,[15,16] we have found a cyclometalated rhodium complex that catalyzes, remarkably, TH of aldehydes around room temperature.

In 2018, our group reported a cyclometalated Cp*Rh(III) complex, a rhodacycle, for catalytic TH of α,β-unsaturated ketones and aldehydes with methanol at 90 °C.[16] Unexpectedly, our further studies showed that the rhodacycle could effect the TH reaction at even room temperature. Given the significance of transferring hydrogen from methanol at room temperature and the easy accessibility of various rhodacycles, we have undertaken further studies to examine the potential of such rhodium complexes for low-temperature TH of carbonyl compounds. Herein, we report the rhodacycle-catalyzed TH of aldehydes with methanol as hydrogen source under ambient reaction conditions.

We initially explored the catalytic TH of 4-bromobenzaldehyde by rhodium complexes using MeOH as both hydrogen donor and solvent. As shown in Table 1, 4-bromobenzyl alcohol was obtained in almost quantitative yield (97%) in the presence of **1** and Na_2CO_3 at 30 °C in 1 h (Table 1, entry 1); the yield decreased only slightly (83%, entry 2) on lowering the temperature to 25 °C, which can be attributed to a reduction in reaction rate at the lower temperature. A similar yield of alcohol product (91%) was obtained for the model reaction in ethanol (Table 1, entry 3). However, surprisingly, no reaction happened when methanol was replaced by isopropanol (Table 1, entry 4).

Next, several rhodacycles were examined using a shorter reaction time (20 min) in methanol as solvent in order to select the most efficient catalyst. The best yield (87%) was obtained using **1**, which bears a hydroxy group at the *para* position to the imino moiety in the ligand (Table 1, entry 5). Notably, replacing the hydroxy group with a hydrogen (**2**) or methoxy group (**3**) led to a lower or no activity at all (Table 1, entry 6-7). A decreased yield was observed when moving the hydroxy group closer to the rhodium centre (**4**, Table 1, entry 8). This is somewhat surprising,

considering that a number of pyridinyl ligands bearing a hydroxy group *ortho* to the metal centre have been shown to be highly effective in dehydrogenation reactions.[13,17] Compared to **1**, complex **5** (Table 1, entry 9) afforded a similar yield, whilst only a trace amount of product was obtained when two methyl groups were introduced (**6**, Table 1, entry 10). These studies established the rhodacycle **1** to be an efficient catalyst for dehydrogenating methanol at room temperature and revealed that the *para*-positioned hydroxy functionality plays a critical promoting role in the catalysis.

Table 1. Optimization of reaction conditions. [a]

Entry	Catalyst	Solvent	Time	Yield %[b]
1	**1**	MeOH	1 h	97
2	**1**	MeOH	1 h	83[c]
3	**1**	EtOH	1 h	91
4	**1**	*i*-PrOH	1 h	N. R.
5	**1**	MeOH	20 min	87
6	**2**	MeOH	20 min	44
7	**3**	MeOH	20 min	N. R.
8	**4**	MeOH	20 min	43
9	**5**	MeOH	20 min	86
10	**6**	MeOH	20 min	< 5

[a] Reaction conditions: 4-bromobenzaldehyde (0.3 mmol), Rh catalyst (1 mol%), K_2CO_3 (0.25 eq.) and MeOH (1.5 mL), stirred at 30 °C. [b] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] Reaction run at 25 °C.

With the optimized reaction conditions in hand, we explored the reaction scope of this new protocol with various aldehyde substrates. As can be seen in Scheme 2, all the substrates were well-tolerated in this reaction system, and the desired aldehyde reduction products were isolated in good to excellent yields. However, substrates bearing electron-withdrawing groups such as nitro, fluoro and trifluoromethyl (**7c**, **7d**, **7h**) afforded slightly lower yields, compared with substrates bearing electron-donating substituents. Notably, high yields were obtained for aldehydes **7g**, **7h**, **7k** and **7l** bearing a sterically bulky group in the *ortho*-position.
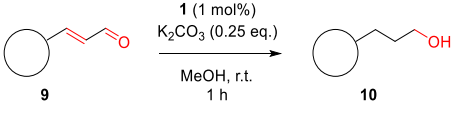
Furthermore, a variety of substrates bearing ester **7j**, aldimine **7n** and ketones **7i** and **7z** were chemoselectively reduced to the corresponding alcohols with the other labile functional groups remaining intact. Heterocyclic aldehydes **7q-7u** and aliphatic aldehydes **7v-7z** could also be transformed to alcohols in high yields.
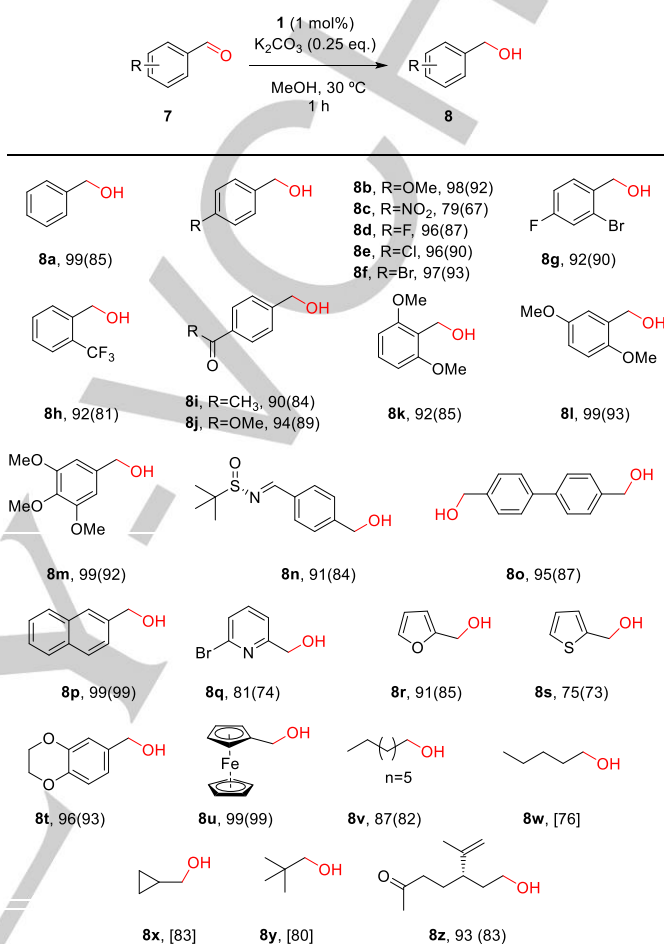
Scheme 2. Transfer hydrogenation of aryl and aliphatic aldehydes. Reaction conditions: aldehyde (0.3 mmol), Rh catalyst **1** (1.0 mmol%), K_2CO_3 (0.25 eq.) and MeOH (1.5 mL), stirred at 30 ºC for 1 h. Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard (values in parentheses are isolated yields), except for **8w**, the yield of which was determined by GC.

The reaction system was successfully extended to a large range of unsaturated aldehydes (Table 2). Taking cinnamaldehyde **9a** as an example, TH of α,β-unsaturated aldehydes under the same conditions as in Scheme 2 affords saturated alcohols, both the C=O and C=C double bonds being reduced. Cinnamaldehydes with electron-donating groups at the *ortho* or *para* position all afforded excellent yields (Table 2, entry 3-5) and, remarkably, TH of cinnamaldehydes with methyl and bulkier phenyl groups at the α carbon also afforded excellent yields, 90 and 99%, respectively (Table 2, entry 6 and 7). Similar results were obtained for aliphatic unsaturated substrates, crotonaldehyde **9h** (2-butenal) and 1-cyclohexene-1-carboxaldehyde **9i** (Table 2, entry 8 and 9), and the catalytic system also tolerated well terpene substrates, citral, perillaldehyde, and steroids, (Table 2, entry 10-15). It is noteworthy, however, that the nonconjugated C=C bonds remained intact in these substrates. To our surprise, ketones in

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**Table 2.** Transfer hydrogenation of unsaturated and other aldehydes. [a]

Entry		Substrate	Product	Yield % [b]
1	9a			81 (79)
2	9b			80 (77)
3	9c			99 (97)
4	9d			99 (95)
5	9e			99 (96)
6	9f			90 (86)
7	9g			99 (96)
8	9h			72 [c]
9	9i			90 (86)
10	9j			99 (92)
11	9k			93 (86)
12	9l			88 (83)
13	9m			99 (98)
14	9n			(52)
15	9o			(48)

[a] Reaction conditions: aldehyde (0.3 mmol), Rh catalyst **1** (1 mmol%), K$_2$CO$_3$ (0.25 eq.) and MeOH (1.5 mL), stirred at 30 ºC for 1 h. [b] Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard; values in parentheses are isolated yields. [c] Yield determined by GC.

the saturated cyclic aldehydes **9n** and **9o**, prepared from steroids like deoxycholic acid and lithocholic acid, could also be reduced under the same condition in fair yields (Table 2, entry 14, 15).[18] In substrate **9n**, only the ketone moiety more remote from the aldehyde group was reduced, while the nearer one was not affected. This may result from the difference in steric hindrance between the two carbonyls, pointing to the potential for selective

reduction of ketone groups in complex substrates with this catalytic protocol. However, it is noted that aromatic ketones, such as acetophenone, could not be reduced at the same condition.

In order to verify that methanol is the only hydrogen source during the TH, the reduction of two aldehydes in deuterated methanol (CD$_3$OD) was carried out. As shown in Scheme 3, incorporation of one deuterium at each aliphatic carbon was observed. This is in line with a mechanistic picture in which β-hydride elimination from MeOH occurs at rhodium to generate a rhodium-hydride, which is transferred *via* the catalyst to the electrophilic carbonyl carbon of a benzaldehyde or to the β carbon of an α,β-unsaturated aldehyde followed by proton and then hydride transfer to afford the saturated product.[15c,16,17a]
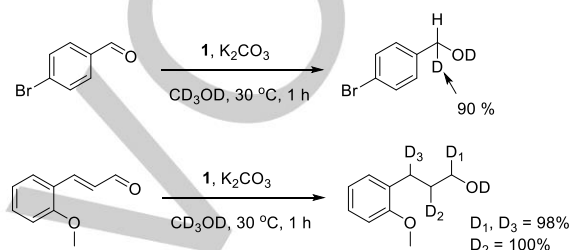
Scheme 3. TH of an aryl and α,β-unsaturated aldehyde with deuterated methanol.
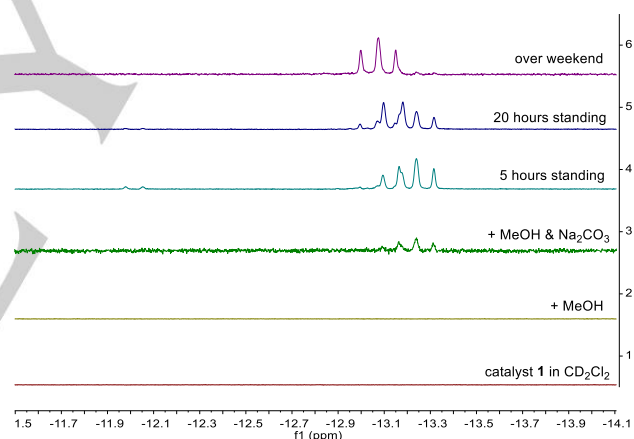
Figure 1. Stacked ^{1}H NMR spectra of the hydride region from the catalyst **1**

To further elucidate the mechanism of the reaction, we examined changes in the hydride region of the ^{1}H NMR spectra of catalyst **1** at room temperature, as shown in Figure 1. No hydride resonance was observed on dissolution of **1** in CD$_2$Cl$_2$ or on introducing a few drops of methanol to the resulting solution. On addition of sodium carbonate (1 equivalent), the yellow CD$_2$Cl$_2$-MeOH solution of **1** turned dark brown immediately. This may indicate either deprotonation of the hydroxy group of the imino ligand or formation of a hydride complex occurs. In support of the latter speculation, a triplet at -13.2 ppm (J_{Rh-H} = 30.3 Hz) appeared in the ^{1}H NMR spectrum, indicative of the formation of a hydride-bridged dimeric rhodium species.[19] As the reaction progressed, a monomeric hydride peak, characterized by a doublet at -12.02 ppm, grew in and then disappeared, and eventually a new dominant triplet arose, indicating the formation of a more stable dimeric rhodium species. Notably, when treated with an aldehyde substrate, this new hydride showed no

observable changes in the ¹H NMR spectrum, suggesting that it is catalytically inactive.

In stark contrast, when the analogous complex **3**, which is inactive in TH under the conditions of Table 1, was treated similarly, no hydride was observed, which highlights the critical role of the *para*-OH moiety of the ligand in facilitating the dehydrogenation of methanol and may explain the lack of catalytic activity of **3**. The importance of this functionality is further seen in the low activity of **6**, in which a methyl is installed between the metal and hydroxy unit. Taken together, these observations suggest that the *para*-OH is involved in the key step of the TH, i.e. methanol dehydrogenation, assisting the dehydrogenation presumably *via* hydrogen bonding.
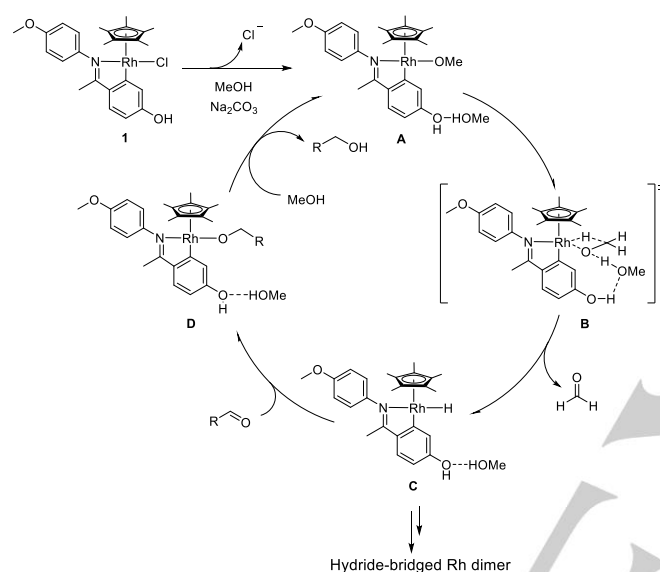
Scheme 4. Proposed mechanism for TH of aldehydes with methanol, featuring hypothetic hydrogen bonding between the ligand, solvent and methoxide.

Based on the above experimental results and previous studies of rhodium-catalyzed TH of carbonyl compounds,[15c,16,17a] a plausible mechanism can be proposed and is shown in Scheme 4. Initially, methanol replaces the coordinated chloride in **1**, generating a rhodium methoxide complex **A**. This is likely to be followed by β-hydride elimination *via* a possible transition state **B**, giving the Rh-H complex **C**. The formation of formaldehyde is confirmed in our previous study.[16a,20,21] Hydride transfer from **C** to the aldehyde leads to the alkoxide complex **D**. Finally, saturated alcohol forms with regeneration of the methoxide complex **A**, closing the catalytic cycle. The added base may facilitate the formation of the methoxide complex or may deprotonate the *para*-OH. Whilst we cannot rule out the possibility of deprotonation, the loss of catalytic activity in **6**, in which the *para*-OH is sterically inaccessible for a transition state like **B**, suggests that deprotonation of the imino ligand, if it occurs, may be less relevant to the catalysis, and what is important is that the OH functionality is properly positioned. We suggest that the *para*-OH engenders a hydrogen bonding network involving a solvent molecule, as illustrated in **B**, thus lowering the energy barrier of β-hydride transfer from MeOH to rhodium and making the low-temperature dehydrogenation possible. Such hydrogen bonding may also facilitate the hydride transfer from **C** to the aldehyde.

Similar interactions have been noted in related studies,[15b,22] and in a very recent theoretical study of the methanol dehydrogenation mechanism, water is shown to play an important role in facilitating the dehydrogenation of both methanol and formaldehyde via hydrogen bonding.[21a] The hydride **C** may give rise to catalytically inactive off-cycle dimeric species, as indicated by the NMR; however, the structure of the species is unclear.

In conclusion, a rhodacycle complex has been found to catalyze highly effective TH of aldehydes at room temperature using methanol as both hydrogen source and solvent. Few molecular catalysts are known of being able to dehydrogenate methanol under such mild conditions. The key to the ability of the identified catalyst is the introduction of a hydroxy functionality and its appropriate positioning in the ligand.

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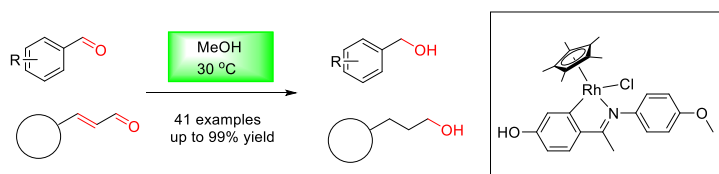
Transferring hydrogen out of methanol near room temperature – a rhodium complex has been found to catalyze transfer hydrogenation of a variety of aldehydes at 25-30 °C, made possible by the *para*-OH functionality on the ligand.

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