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Selective Acceptorless Conversion of Primary Alcohols to Acetals and Dihydrogen Catalyzed by the Ruthenium(II) Complex $Ru(PPh_3)_2(NCCH_3)_2(SO_4)$

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Abstract: The complex bis(acetonitrile)bis(triphenylphosphine)ruthenium(II) sulfate $[Ru(PPh_3)_2(NCCH_3)_2(SO_4)]$, fully characterized spectroscopically and by a single crystal X-ray study, catalyzes at 110 °C the direct transformation of primary alcohols to the corresponding acetals with liberation of molecular hydrogen. The formation of acetals proceeds *via* direct substitution of the hydroxy group of the hemiacetal intermediate by an alcohol molecule. The closely related bis(triphenylphosphine)ruthenium(II) acetate $[Ru(PPh_3)_2(OAc)_2]$ catalyzes the conversion of primary alcohols to the corresponding esters rather than acetals.

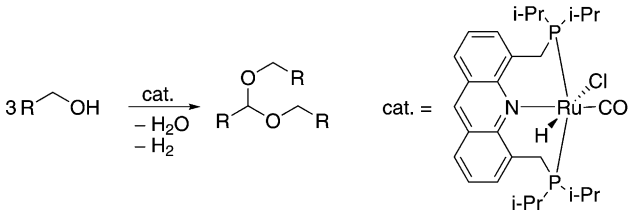
Keywords: alcohols; dehydrogenation; homogeneous catalysis; ruthenium; transition metals

Introduction

The atom-efficient and environmentally benign catalytic oxidation of alcohols to various carbonyl compounds is of much industrial interest.[1–4] Particularly desirable is the homogeneous selective alcohol dehydrogenation with evolution of molecular hydrogen.[5–12]

Acetals are usually prepared by condensation of aldehydes with alcohols, catalyzed by various catalysts, including protic[13] or Lewis[14] acids. The direct conversion of alcohols to the corresponding acetals is an attractive reaction, due to its high atom economy and circumventing the need for aldehydes or aldehyde derivatives.

To the best of our knowledge, there are only three reported homogeneous catalysts for the direct transformation of primary alcohols to acetals and molecular hydrogen.[11,12,15] In 1987, Murahashi et al.[12] reported the $Ru(PPh_3)_3Cl_2$-catalyzed conversion of 1-hexanol to 1,1-bis(hexyloxy)hexane in 8 turnovers at 180 °C after 4 h under Ar, together with the formation of hexyl hexanoate. In 2000, Thorp et al.[15] reported the conversion of ethanol to the acetal + acetaldehyde (total of 30 turnovers) catalyzed by $Re(4\text{-}NC_6H_4Cl)Cl_3(PPh_3)_2$ + 8 dppe, after 48 h reflux in 95% ethanol under Ar. An acridine-based pincer catalyst (Scheme 1) was reported by our group in 2009.[11] Heating 0.1 mol% catalyst solution in either neat 1-hexanol (157 °C, oil bath temperature) or 1-pentanol (bp 138 °C, reflux) under Ar for 72 h yielded 81.5% and 92% of the corresponding acetals, respectively.

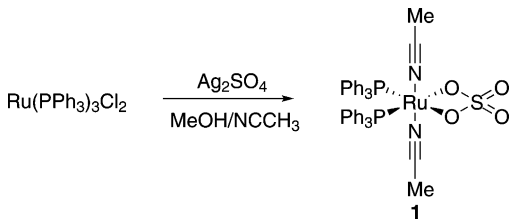


Scheme 1. Conversion of primary alcohols to acetals and H_2 catalyzed by an acridine-based pincer catalyst.

In this paper, we describe a ruthenium complex based on simple commercially available ligands, which efficiently and selectively catalyzes dehydrogenation of primary alcohols to acetals and H_2 in high turnover numbers and good selectivity under mild conditions. The simple catalyst structure and its easy synthesis, along with its efficiency, make it particularly attractive.

Results and Discussion

The new $Ru(PPh_3)_2(NCCH_3)_2(SO_4)$ (**1**) was prepared by reaction of $Ru(PPh_3)_3Cl_2$ with Ag_2SO_4 in a solution of acetonitrile and methanol (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of **1** exhibits a singlet at 52.47 ppm. The methyl groups of acetonitrile give rise



Scheme 2. Synthesis of complex **1**.

to singlets at 1.94 and 4.20 ppm in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, respectively. A single crystal X-ray study of **1** reveals a distorted octahedral structure with two acetonitrile molecules coordinated *trans* to each other (Figure 1). The deviation from an idealized octahedral geometry is due to the small bite angle of the SO_4 ligand.

Complex **1** catalyzes dehydrogenation of primary alcohols to acetals (Table 1). In reactions at elevated temperatures poor selectivity was observed, and the product acetal was accompanied by formation of the corresponding dialkyl ether when either 1-hexanol (bp 157 °C) or 1-pentanol (bp 138 °C) was refluxed in the presence of 0.1 mol% of **1**. However, **1** exhibited excellent selectivity at 118 °C (Table 1, entry 1) giving a 47% yield of 1,1-bis(butyloxy)butane acetal upon refluxing with 1-butanol for 48 h. Longer reaction times did not result in further increases of the acetal yield (Table 1, entry 2). Instead, the formation of dibutyl ether was observed, probably due to catalyst decomposition.

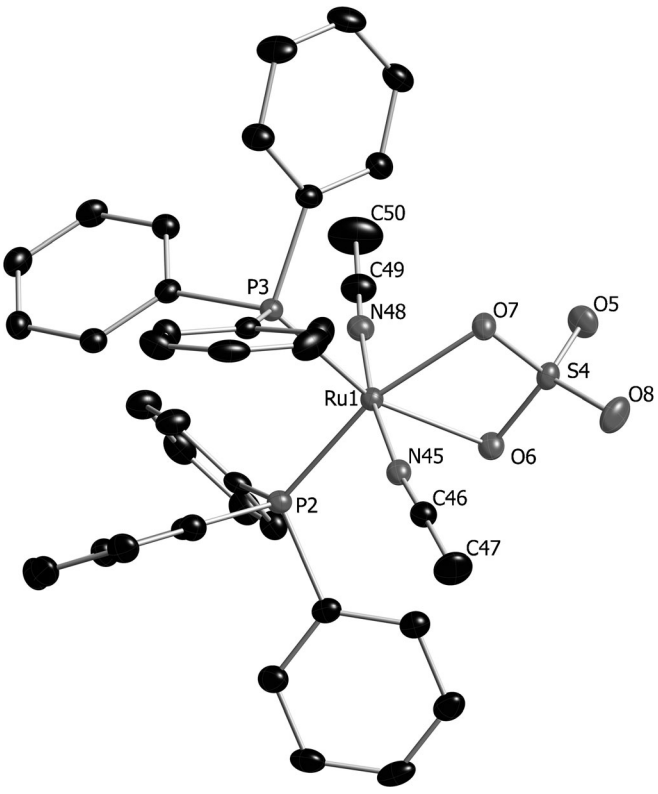


Figure 1. Molecular structure of complex **1** at 50% probability level. Selected bond lengths (Å) and angles (°): Ru1–P2 2.2944(5), Ru1–P3 2.3022(4), Ru1–O6 2.1496(12), Ru1–O7 2.1631(12), Ru1–N45 2.0106(14), Ru1–N48 2.0094(15); O6–Ru1–O7 66.27(4), P2–Ru1–P3 98.546(16), N45–Ru1–N48 172.75(6), P2–Ru1–O7 165.14(3), P3–Ru1–O6 161.35(4)°.

Addition of toluene as a solvent (Table 1, entry 3) improved alcohol conversion and the yield of the corresponding acetal, but led to lower reaction selectivity. Namely, 48 h reflux of a toluene solution of 1-hexanol in the presence of 0.1 mol% of **1** led to 75% conversion of 1-hexanol primarily to 1,1-bis-(hexyloxy)hexane (61%). Formation of the acetal was accompanied by the appearance of multiple minor products. Longer reaction times did not result in further alcohol conversion, likely indicating catalyst decomposition (Table 1, entry 4).

Higher catalyst/alcohol ratios resulted in more than 90% conversion, mostly to the corresponding acetals (Table 1, entries 5 and 6). It is noteworthy that the reported acridine-based pincer catalyst (Scheme 1) was inactive at 118 °C or lower temperatures.[11]

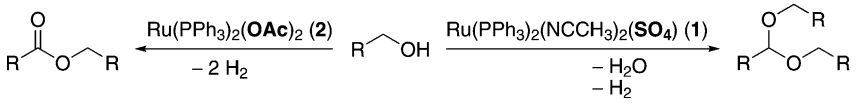
It is likely that **1** mediates the dehydrogenation of alcohols to give the corresponding aldehydes and H_2 (Scheme 3). Formation of hydrogen gas was detected by gas chromatography. Once formed, the aldehyde reacts with excess of alcohol to give a hemiacetal. Then acetal formation may be involved either *via* formation of a vinyl ether intermediate (Scheme 3, route A)[11] or *via* direct substitution of the hydroxy group of the hemiacetal by an alcohol molecule (Scheme 3, route B). In the later route the catalyst may act as a Lewis acid. Lewis acids were reported as catalysts for the condensation of aldehydes with alcohols to produce acetals.[14]

Utilization of a substrate lacking β-hydrogens, which is not capable of formation of a vinyl ether, can differentiate between these two pathways.

For this purpose benzyl alcohol was refluxed at 110 °C in the presence of **1** (0.286 mol%), leading to formation of benzaldehyde (4%), benzaldehyde dibenzyl acetal (59%) and dibenzyl ether (15%) (Table 1, entry 7). Formation of benzaldehyde dibenzyl acetal indicates that the direct substitution of the hydroxy group of the hemiacetal by an alcohol molecule is operative, at least in this case (Scheme 3, route B). Dibenzyl ether formation can be explained by the same mechanism of direct substitution of the hydroxy group of benzyl alcohol by an alcohol molecule. The benzyl cation is much more stable than a primary alkyl cation, therefore the formation of dialkyl ether was insignificant with aliphatic alcohols under identical conditions.

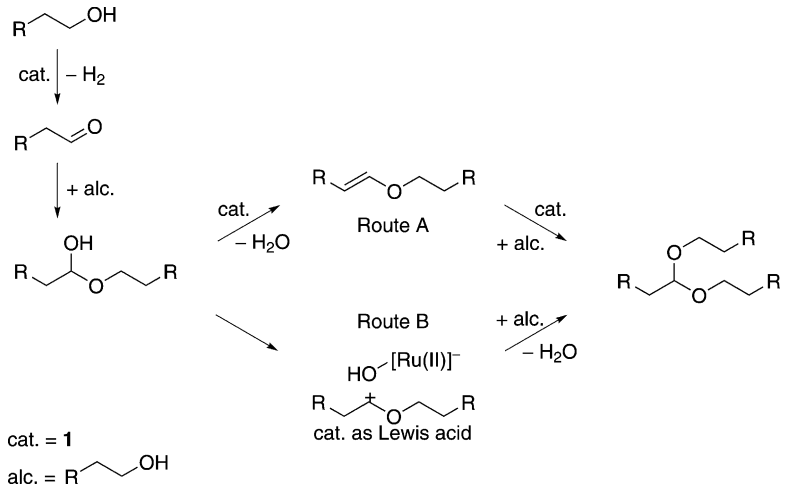
It is noteworthy that unlike the current reaction, the acridine-based pincer-type catalyst reported by our group[11] (Scheme 1) catalyzed the conversion of

Table 1. Direct transformation of primary alcohols to acetals and esters catalyzed by $Ru(PPh_3)_2(NCCH_3)_2(SO_4)$ (**1**) and $Ru(PPh_3)_2(OAc)_2$ (**2**).[a]

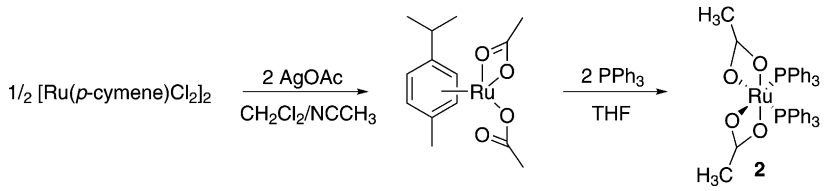


Entry	Catalyst	Amine, equiv./Ru	Alcohol	Equiv./catalyst	Temperature [°C]	Time [h]	Conversion [%]	Yield [%][b]		
								Aldehyde	Ester	Acetal
1	**1**	–	1-butanol	1000	118	48	55[c]	4	0	47
2	**1**	–	1-butanol	1000	118	73	74[d]	3	<1	44
3	**1**	–	1-hexanol	1000	110[e]	48	75	<1	0	61
4	**1**	–	1-hexanol	1000	110[e]	72	77	<1	0	63
5	**1**	–	1-hexanol	350	110[f]	48	96	1	0	73
6	**1**	–	1-pentanol	350	110[f]	48	94	1	0	72
7	**1**	–	benzyl alcohol	350	110[f]	48	80[g,h]	4[g]	0	59[i]
8	**2**	–	1-butanol	1000	118	48	19	10	7	0
9	**2**	–	1-pentanol	1000	138	48	20	9	10	<1
10	**2**	–	1-hexanol	1000	157	48	46	3	39	3
11	**2**	$N(n\text{-}Bu)_3$, 10	1-hexanol	1000	157	48	48	3	44	0
12	**2**	TEEDA, 5	1-hexanol	1000	157	48	56	6	49	0
13	**2**	TEEDA, 20	1-hexanol	1000	157	48	70	1	69	0
14	**1**	$N(n\text{-}Bu)_3$, 2	1-hexanol	1000	157	48	56	5	12	37
15	**1**	TEEDA, 10	1-hexanol	1000	157	48	21	<1	19	0

[a] 0.01 mmol of catalyst and the marked equivalents of alcohol were refluxed under Ar flow.
[b] Yields and conversions (average of 2–4 runs) were determined by GC unless stated otherwise. When the sum of the values is less than 100%, other products were observed in small amounts.
[c] 1–2% of dibutyl ether was formed.
[d] *Ca.* 12% of dibutyl ether was formed together with multiple minor products.
[e] Toluene (2 mL) was added, and the solution was refluxed.
[f] Toluene (1 mL) was added, and the solution was refluxed.
[g] Determined by HPLC.
[h] *Ca.* 15% were converted to dibenzyl ether, determined by ^1H NMR.
[i] Determined by ^1H NMR.



Scheme 3. Proposed pathways for acetalization.



Scheme 4. Synthesis of **2**.

primary alcohols to acetals by the vinyl ether pathway (Scheme 3, route A), which consequently led to formation of benzyl benzoate from benzyl alcohol, rather than the corresponding acetal.

We have next examined the closely related complex $Ru(PPh_3)_2(OAc)_2$ (**2**) as a catalyst for the dehydrogenation of primary alcohols. Although **2** has been known for decades,[16a] to the best of our knowledge, its ability to catalyze the dehydrogenation of primary alcohols has not been explored.[17] Here we present an alternative procedure for the preparation of **2**. For this purpose, $[Ru(p\text{-cymene})Cl_2]_2$ was reacted with four equivalents of AgOAc to give Ru(*p*-cymene)-$(OAc)_2$[18] (Scheme 4). Red prismatic crystals of Ru(*p*-cymene)$(OAc)_2$ were obtained from Et_2O/hexane (v/v 1/1) solution. A single crystal X-ray study of Ru(*p*-cymene)$(OAc)_2$ (Figure 2) revealed a mononuclear complex with a η^6-*p*-cymene ligand and two acetate moieties, one η^1-OAc and another η^2-OAc, coordinated to ruthenium. The distance between the ruthenium atom and the aromatic ring was calculated to be 1.627(9) Å.

Ru(*p*-cymene)$(OAc)_2$ was reacted with two equivalents of PPh_3 to give complex **2** (Scheme 4). The structure of **2** was recently reported by Lynam et al.[16b]

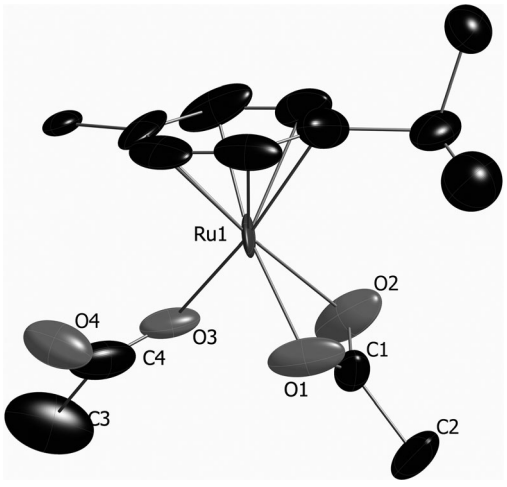


Figure 2. Molecular structure of [Ru(*p*-cymene)$(OAc)_2$] at 50% probability level. Ru1–O1 2.193(6), Ru1–O2 2.111(7), Ru1–O3 2.047(10), O1–C1 1.211(10), O2–C1 1.270(10), O3–C4 1.184(17), O4–C4 1.373(16) Å; O1–C1–O2 120.5(7), O3–Ru1–O2 77.5(4), O3–Ru1–O1 87.7(3), O2–Ru1–O1 60.0(2)°.

Refluxing of 1-butanol (bp 118 °C) for 48 h in the presence of 0.1 mol% of **2** led to 19% conversion to butyl butyrate (7%) and butyraldehyde (10%) (Table 1, entry 8). Similar results (20% conversion) were obtained when 1-pentanol (bp 138 °C) was refluxed for 48 h in the presence of 0.1 mol% of **2** (Table 1, entry 9). The catalytic activity of **2** increased with increasing the temperature to 157 °C. Thus, refluxing 1-hexanol (bp 157 °C) for 48 h in the presence of 0.1 mol% of **2** gave 46% conversion, primarily to hexyl hexanoate, 39% (Table 1, entry 10).

The addition of amines had a positive effect on the reactivity and selectivity of catalyst **2** towards ester formation. No acetal was formed in the presence of amines (Table 1, entries 11–13). Slightly greater conversion (56%) was achieved in the presence of the chelating amine tetraethylethylenediamine (TEEDA), than in the presence of the monodentate amine (48%), although the same N/Ru ratio was kept (Table 1, entries 12 and 11, respectively). Catalyst efficiency was further improved by increasing the amount of TEEDA. Namely, 70% of 1-hexanol was selectively converted to hexyl hexanoate (69%) in the presence of 20 equivalents of TEEDA.

So far, the most efficient homogeneous catalyst for the direct conversion of primary alcohols to *esters* and molecular hydrogen was developed by our group.[8a] The ruthenium complex bearing a *t*-Bu-PNN pincer ligand achieved 92% conversion of 1-hexanol to hexyl hexanoate after 2.5 h under the same conditions as used for the catalytic reaction described in the Table 1, entry 10. Although catalyst **2** is much less active than the *t*-Bu-PNN pincer catalyst, it still may be useful owing to its selectivity in the presence of amines (Table 1, entries 11–13) and its structural simplicity.

Addition of amines had a significant effect on the reactivity of **1** as well. As mentioned above, catalyst **1** showed poor selectivity at 157 °C, and formation of bis-hexyloxyhexane was accompanied by formation of a significant amount of dihexyl ether together with multiple minor products. Addition of two equivalents of $N(n\text{-Bu})_3$ to the reaction mixture suppressed the formation of dihexyl ether (Table 1, entry 14). Interestingly, addition of a greater amount of amine (10 equivalents of TEEDA) resulted in a reactivity

'switch' to hexyl hexanoate as the major product (Table 1, entry 15).

Although both catalysts $Ru(PPh_3)_2(NCCH_3)_2(SO_4)$ (**1**) and $Ru(PPh_3)_2(OAc)_2$ (**2**) are based on the $Ru(II)(PPh_3)_2$ moiety, there are two major differences between them. First, the sulfate counter-anion is expected to make **1** a stronger Lewis acid. Secondly, acetonitrile is more prone to dissociate than the η^2-acetate, thus providing a potential vacant coordination site.

The formation of ester and not acetal by **2** may be a result of lack of an accessible coordination site, which is required for coordination of the hemiacetal to the Lewis-acidic complex (Scheme 3, route B). In the case of compound **1**, the vacant site can be easily provided by acetonitrile dissociation. Suppression of acetal formation by addition of amines to the reaction mixture (Table 1, entry 15) is in accord with the above explanation of the dependence of acetal formation on the availability of a vacant coordination site.

Conclusions

$Ru(PPh_3)_2(NCCH_3)_2(SO_4)$ (**1**) efficiently catalyzes the direct conversion of alcohols to acetals, H_2 and water. It is likely that acetal formation involves direct substitution of the hydroxy group of a hemiacetal intermediate by an alcohol molecule. This step in the catalytic cycle seems to be dependent on the availability of a coordination site on the ruthenium center, which acts as a Lewis acid. Such an explanation is supported by two observations. First, **1** catalyzed the conversion of 1-hexanol to hexyl hexanoate in the presence of 10 equivalents of TEEDA. Next, $Ru(PPh_3)_2(OAc)_2$ (**2**) catalyzed the conversion of primary alcohols to the corresponding esters as a result of the strong η^2-coordination of acetate.

This work presents an efficient and selective catalyst for the direct conversion of primary alcohols to acetals and molecular hydrogen. Catalyst **1** is efficient at much lower temperatures (110 °C) than the acridine-based pincer catalyst reported earlier.[11] Moreover, **1** is based on simple and commercially available ligands, making it especially attractive.

Experimental Section

General Procedures

Metal complexes were prepared and the catalytic reactions were set under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with an MO 40–2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. Dichloromethane (HPLC grade) was used as received. All alcohols were refluxed over sodium and distilled under an argon atmosphere. All non-deuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glove box over 4 Å molecular sieves. Commercially available reagents were used as received. $RuCl_2(PPh_3)_3$ was prepared according to a literature procedure.[19]

^1H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded at 400, 100, 162, and 376 MHz, respectively, using a Bruker AMX-400 NMR spectrometer. All spectra were recorded at 292 K, unless otherwise noted. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to the residual signals of an appropriate deuterated solvent. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. The IR spectra were measured on a Nicolet Protegé 460 FTIR; the sample solution was placed on NaCl disk, and the solvent was allowed to evaporate to form a film.

Elemental analyses (C, H, N) were performed on a CHN elemental analyzer (FlashEA 1112, Eager 300 Software). GC measurements were performed using a Carboxen 1000 column on an HP 690 series GC system. The eluent gas was helium. GC/MS measurements were performed using an instrument consisting of an HP 5973 mass-selective detector and an HP 6890 GC. A 5% phenylmethylsilicone 0.32 mm i.d., 0.25 μm coating, 30-m length column (Restek 5MS). The eluent gas was helium. HPLC measurements were performed using a reverse-phase LiChrospher 100 RP-18 column (5 μm) 250–4 on a Hitachi system (pump L-7100, UV detector L-7400). Electrospray ionization (ESI) mass spectrometry was performed using a Micromass Platform instrument.

Single crystal X-ray analyses data were collected with Bruker APEX-II KappaCCD diffractometer at 100(2) K, MoKα ($\lambda = 0.71073$ Å), graphite monochromator. The data were processed with APEX-II package programs. Structures were solved by direct methods with AUTOSOLVE module and refined with full matrix least-squares refinement based on F^2 by SHELXL-97. CCDC 840256 and CCDC 840257 contain the supplementary crystallographic data for compounds **1** and [Ru(*p*-cymene)$(OAc)_2$], respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

$Ru(PPh_3)_2(NCCH_3)_2(\eta^2\text{-}SO_4)$ (1)

A yellow solution of $Ru(PPh_3)_3Cl_2$ (200 mg, 0.208 mmol) in methanol (5 mL) and acetonitrile (5 mL) was poured on Ag_2SO_4 (65 mg, 0.208 mmol). Ag_2SO_4 has limited solubility under the reaction conditions;[20] therefore, the reaction mixture was well-stirred at ambient temperature for 28 h. The resulting suspension was filtered through celite and the solvent was evaporated. The resulting yellow solid was washed with THF (2 × 2 mL), then dissolved in CH_2Cl_2 (10 mL) and filtered through a cotton pad. The solution was concentrated to 2 mL under vacuum followed by addition of 2 mL of diethyl ether. The solution was left overnight at ambient temperature, resulting in precipitation of a crystalline yellow solid. The mother liquor was decanted and the precipitate was dried under vacuum to give the product as a yellow

crystalline material; yield: 137 mg (82%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 52.47$ (s, PPh_3); ^1H NMR (CD_2Cl_2): $\delta = 7.38$ (m, Ph, *para* to P, 6H), 7.23 (m, Ph, 12H), 7.17 (m, Ph, 12H), 1.94 (s, NCCH_3, 6H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta =$ 134.50 (d, $^1J_{P,C} = 20.8$ Hz, PPh_3), 134.31 (d, $^1J_{P,C} = 20.8$ Hz, PPh_3), 134.17 (vt, $^2J_{P,C} = 4.94$ Hz, PPh_3), 130.15 (s, PPh_3), 128.31 (vt, $^3J_{P,C} = 4.86$ Hz, PPh_3), 122.97 (s, N*C*CH$_3$), 4.20 (s, NC*C*H$_3$); confirmed by DEPT; elemental analysis (%) found (calcd.): C 59.36 (59.77), H 4.52 (4.51), N 3.49 (3.49); IR (film): $\nu = 1229$ ($\nu_{S=O}$), 1136 ($\nu_{S=O}$), 1093 (ν_{S-O}), 919 (ν_{S-O}) cm^{-1}.

X-Ray Analysis of $Ru(PPh_3)_2(NCCH_3)_2(\eta^2\text{-}SO_4)$ (1)

Light yellow prismatic crystals suitable for a single crystal X-ray analysis were obtained by recrystallization of 60 mg of **1** from CH_2Cl_2/Et_2O (2 mL/2 mL) solution. Crystal data: $[C_{40}H_{36}N_2O_4P_2Ru_1S_1 + C_1H_2Cl_2]$, $0.40 \times 0.13 \times 0.08$ mm^3, monoclinic, $P2_1/c$, $a = 14.6022(4)$, $b = 11.6721(3)$, $c =$ 24.1771(7) Å, $\beta = 106.280(2)°$, from 60894 reflections, $T =$ 100(2) K, $V = 3955.5(2)$ Å^3, $Z = 4$, Fw = 888.70 g mol^{-1}, $\rho_{calcd.} = 1.492$ Mg m^{-3}, $\mu = 0.709$ mm^{-1}. Data collection and processing: $-22 \le h \le 22$, $-18 \le k \le 16$, $-36 \le l \le 36$, frame scan width = 0.5°, scan speed 1.0° per 60 sec, typical peak mosaicity 0.72°,60890 reflections collected, 15638 independent reflections (R-int = 0.0471). Solution and refinement: 480 parameters with no restraints, final $R_1 = 0.0361$ (based on F^2) for data with $I > 2\sigma(I)$ and, $R_1 = 0.0587$ on 15010 reflections, goodness-of-fit on F$^2 = 1.008$, largest electron density peak = 1.056 e Å^{-3}, deepest hole = −0.957 e Å^{-3}.

Ru(*p*-cymene)$(OAc)_2$

Ru(*p*-cymene)$(OAc)_2$ was prepared using the procedure described by Stephenson and Bennett.[18] To a solution of $[Ru(p\text{-cymene})Cl_2]_2$ (35 mg, 0.0572 mmol) in benzene (6 mL) was added AgOAc (40.1 mg, 0.240 mmol). The reaction mixture was left stirring for 24 h at ambient temperature, with exclusion of light. The resulting suspension was filtered through celite to give a clear orange solution and the solvent was evaporated to give an orange solid. The product was recrystallized from a solution of Et_2O/hexane (1.7 mL/1.7 mL) within 2 days. The mother liquor was decanted and the resulting orange crystalline material was dried under vacuum to give the product, Ru(p-cymene)$(OAc)_2$; yield: 32.3 mg (80%). ^1H NMR (CD_2Cl_2): $\delta = 5.74$ (d, $^3J_{H,H} =$ 4.8 Hz, *p*-cymene, Ar, 2H), 5.52 (d, $^3J_{H,H} = 4.8$ Hz, *p*-cymene, Ar, 2H), 2.81 [sept, $^3J_{H,H} = 6.9$ Hz, *p*-cymene, *i*-Pr, C*H*-(CH$_3$)$_2$, 1H], 2.20 (s, *p*-cymene, Me, CH_3, 3H), 1.84 (s, acetate, CH_3, 6H), 1.33 [d, $^3J_{H,H} = 6.9$ Hz, *p*-cymene, *i*-Pr, CH-(CH_3)$_2$, 6H]; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 184.05$ [s, acetate, -*C*(O)O-], 98.03 (s, *p*-cymene, Ar), 93.04 (s, *p*-cymene, Ar), 79.28 (s, *p*-cymene, Ar, *C*H), 77.84 (s, *p*-cymene, Ar, *C*H), 31.81 [s, *p*-cymene, *i*-Pr, -*C*H(CH$_3$)$_2$], 23.84 [s, acetate, -C(O)O-*C*H$_3$], 22.56 [s, *p*-cymene, *i*-Pr, -CH(*C*H$_3$)$_2$], 18.68 (s, *p*-cymene, Me, *C*H$_3$), confirmed by DEPT, HSQC; elemental analysis (%) found (calcd.): C 48.06 (47.58), H 5.77 (5.70).

X-Ray Structural Analysis of Ru(*p*-cymene)$(OAc)_2$

Ru(*p*-cymene)$(OAc)_2$ (5 mg) was dissolved in Et_2O (0.8 mL), then hexane (0.8 mL) was added. Red tetragonal crystals appeared in a few days. Crystal data: $C_{14}H_{20}O_4Ru_1$, $0.2 \times 0.2 \times 0.3$ mm^3, tetragonal, $P4_32_12$, $a = 10.6310(2)$, $c =$ 25.2855(12) Å, from 20 degrees of data, $T = 100(2)$ K, $V =$ 2857.72(16) Å^3, $Z = 8$, Fw = 353.37 g mol^{-1}, $\rho_{calcd.} =$ 1.643 Mg m^{-3}, $\mu = 1.104$ mm^{-1}. Data collection and processing: $-13 \le h \le 12$, $-13 \le k \le 13$, $-31 \le l \le 31$, frame scan width = 0.5°, scan speed 1.0° per 40 sec, typical peak mosaicity 0.645°, 57713 reflections collected, 4569 independent reflections (R-int = 0.0733). Solution and refinement: 250 parameters with 48 restraint, final $R_1 = 0.0516$ (based on F^2) for data with $I > 2\sigma(I)$ and, $R_1 = 0.0553$ on 2923 reflections, goodness-of-fit on F$^2 = 1.181$, largest electron density peak = 0.619 e Å^{-3}, deepest hole = −0.673 e Å^{-3}.

$Ru(PPh_3)_2(OAc)_2$ (2)

This compound was reported.[16] Here we present an alternative preparation. A solution of $[Ru(p\text{-cymene})Cl_2]_2$ (30 mg, 0.0490 mmol) and AgOAc (32.7 mg, 0.196 mmol) in a mixture of CH_2Cl_2 (3 mL) and acetonitrile (3 mL) was stirred at ambient temperature for 25 h. The resulting suspension was filtered through celite and the solvent was evaporated. The resulting orange solid was dissolved in THF (5 mL), followed by addition of PPh_3 (54 mg, 0.206 mmol) and stirring at ambient temperature for 11 h, upon which the orange colour became deeper. The THF was evaporated and the resulting orange solid was dissolved in CH_2Cl_2 (10 mL) and filtered through a cotton pad. The solution was concentrated to 2 mL under vacuum, and then 2 mL of diethyl ether were added. The solution was left overnight at ambient temperature, resulting in precipitation of red crystals. The mother liquor was decanted, and the crystals were washed with diethyl ether (1 mL) and dried under vacuum to give the product as a red crystalline material; yield: 59 mg (73%, for **2**·CH_2Cl_2). Elemental analysis for **2**·CH_2Cl_2 (%) found (calcd): C 59.51 (59.43), H 4.62 (4.62).

Typica1 Procedures for Catalytic Dehydrogenation of Primary Alcohols

Reactions of **1** and **2** with primary alcohols under various conditions are summarized in Table 1. The reactions were performed under an argon flow. Exposure to oxygen resulted in reduced catalyst reactivity.

Table 1, entries 1, 2 and 8–15: The catalyst (0.01 mmol), alcohol (10 mmol) and the specified amount of the amine were placed in a Schlenk flask equipped with a condenser. The reaction mixture was refluxed in an open system under an argon flow for the specified time.

Table 1, entries 3 and 4: Catalyst **1** (8.0 mg, 0.01 mmol), 1-hexanol (1.255 mL, 10 mmol) and toluene (2 mL) were placed in a Schlenk flask equipped with a condenser. The reaction mixture was refluxed in an open system under an argon flow for the specified time.

Table 1, entries 5–7: Catalyst **1** (8.0 mg, 0.01 mmol), the alcohol (3.5 mmol) and toluene (1 mL) were placed in a Schlenk flask equipped with a condenser. The reaction mixture was refluxed in an open system under an argon flow for 48 h.

After cooling to room temperature, the alcohols (1-hexanol, 1-pentanol and 1-butanol) and the corresponding aldehydes, ethers, esters and acetals were quantitatively determined by GC using toluene, *m*-xylene or mesitylene as inter-

nal standards. Signal identity was confirmed by GC/MS. Formation of acetals was further confirmed by ^{1}H NMR and ESI-MS. The amounts of benzyl alcohol and benzaldehyde were determined by HPLC. HPLC conditions were: flow rate = 1 mL min^{-1}, injection volume = 20 μL, detector wavelength = 254 nm. Mobile phase was 70:30 acetonitrile:H_2O. Samples were prepared as follows: the reaction mixture was cooled down, treated with hexane (10 mL) and left at −20 °C for several days to precipitate the catalyst. The hexane solution was extracted with 50 mL of acetonitrile (sample A). Sample B was prepared by two-fold dilution of the sample A. Retention times: benzyl alcohol, 2.6 min; benzaldehyde, 3.2 min; dibenzyl ether, 6.6 min; benzaldehyde dibenzyl acetal, 11.9 min. After conducting HPLC measurements, samples A and B were unified, volatiles were evaporated and the yields of dibenzyl ether and benzaldehyde dibenzyl acetal were determined by ^{1}H NMR with mesitylene as the internal standard.

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