Improved Efficiency of the Ruthenium-Catalyzed Redox Isomerization of Allyl Alcohols

Christian Slugovc, Eva Rüba, Roland Schmid, and Karl Kirchner*,†

Institute of Inorganic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria

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Summary: The new complexes [RuCp(PR$_3$)(CH$_3$CN)$_2$]PF$_6$ (R = Ph, Me, Cy) are highly active catalysts for the redox isomerization of allyl alcohols to give the corresponding carbonyl compounds in high yields and high efficiency. All reactions proceed under mild reaction conditions. In some cases, allylations of the carbonyl compounds could be achieved in a tandem catalytic process.

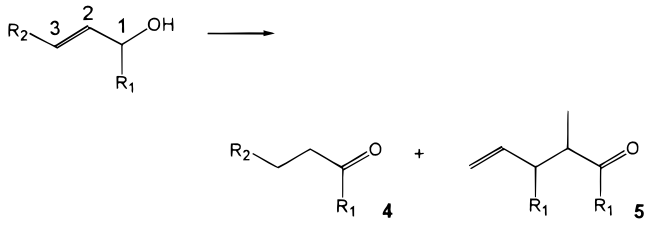
Introduction

Recently Kulawiec and Trost have shown[1] that the isomerization of allyl alcohols to the corresponding carbonyl compounds is catalyzed by RuCp(PPh$_3$)$_2$Cl in the presence of NH_4PF_6. However, the catalyst is substitutionally inert, such that in addition to high temperatures (typically 100 °C in dioxane as the solvent) also high concentrations of both a chloride scavenger (10 mol %) and the catalyst (5 mol %) have been used. Furthermore, it appears to be difficult to modify the steric and electronic properties of the catalyst in a simple and systematic way. In an attempt to improve the performance, we have prepared a series of substitutionally labile complexes of the type [RuCp(PR$_3$)(CH$_3$CN)$_2$]$^+$, which straightforwardly generate the pseudo-14e fragment [RuCp(PR$_3$)]$^+$.[2] Herein we report on the redox isomerization of some allyl alcohols catalyzed by the new highly reactive cationic complexes [RuCp(PR$_3$)(CH$_3$CN)$_2$]PF$_6$ (R = Ph (**1**), Me (**2**), Cy (**3**)). Moreover, we describe a catalytic "tandem reaction" of allyl alcohols to give γ,δ-unsaturated carbonyl compounds via allylation of the redox isomerization products.

Results and Discussion

The complexes [RuCp(PR$_3$)(CH$_3$CN)$_2$]PF$_6$ (**1**−**3**) have been prepared by reacting [RuCp(CH$_3$CN)$_3$]PF$_6$[3] with 1 equiv of PR$_3$ in quantitative yield. Treatment of **1**−**3** (1 mol %) with allyl alcohols in $CDCl_3$ at ∼57 °C affords the corresponding carbonyl compounds **4** and in some cases, as monitored by ^{1}H NMR spectroscopy, also the coupling products **5** (Table 1). Even at about 40−50 °C, acetonitrile is released from the complex, forming the catalytically active species (after 10 min at 45 °C resonances of **4** and **5** could be already detected by ^{1}H NMR). C^1-substituted allyl alcohols react much more quickly than those featuring substituents at the C^3 carbon atom. It is interesting to note that both the conversion and product distribution depend on the nature of the phosphine ligand (see below). In line with the report of Kulawiec and Trost, we have found that neither C^1- and C^3-disubstituted allyl alcohols nor primary alcohols without an allyl group such as geraniol, 2-methyl-3-buten-2-ol, 3-buten-1-ol, and ethanol are converted under these conditions.

Table 1. Reaction of Allyl Alcohols in the Presence of the Precatalysts 1−3[a]



					amt, %	
entry	catalyst	time	R_1	R_2	**4**	**5**
1	**1**	10 min	H	H	82	7
2	**2**	15 min	H	H	67	21
3	**3**	3 min	H	H	86	4
4	**1**	3 min	Me	H	>98	
5	**2**	5 min	Me	H	>98	
6	**3**	3 min	Me	H	>98	
7	**1**	30 min	4-MeC$_6$H$_4$	H	23	74
8	**2**	8 min	4-MeC$_6$H$_4$	H	60	38
9	**3**	5 min	4-MeC$_6$H$_4$	H	67	29
10	**1**	17 h	H	Ph	91[b]	
11	**2**	15 h	H	Ph	87[b]	
12	**3**	17 h	H	Ph		
13	**1**	3 min	*n*-Hex	H	>98	
14	**2**	90 min	*n*-Hex	H	>98	
15	**3**	3min	*n*-Hex	H	>98	

[a] All reactions performed in $CDCl_3$ (1 mol % catalyst) at 57 °C in a sealed NMR tube. Allyl alcohols are quantitatively consumed in all reactions. [b] Yield after chromatographic workup.

To optimize the results of the NMR experiments, neat 2-propenol was reacted with 0.03 mol % of **3** by slowly raising the temperature to 80 °C. A vigorous reaction occurred at ∼68 °C (measured in the flask). After the reaction mixture was kept at this temperature for 10 min, the propanal (bp 47 °C) formed was collected by distillation in 60% yield. However, in the residue there were no longer resonances of allylic hydrogen atoms detectable by ^{1}H NMR spectroscopy, indicating complete consumption of 2-propenol but formation of oligo- and polymeric propanal (if less than 0.03 mol % catalyst is used, the reaction is incomplete). Thus, under these reaction conditions, the formation of **5a** is completely suppressed. The turnover number (TON) and turnover

† E-mail: kkirch@mail.zserv.tuwien.ac.at.

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Scheme 1

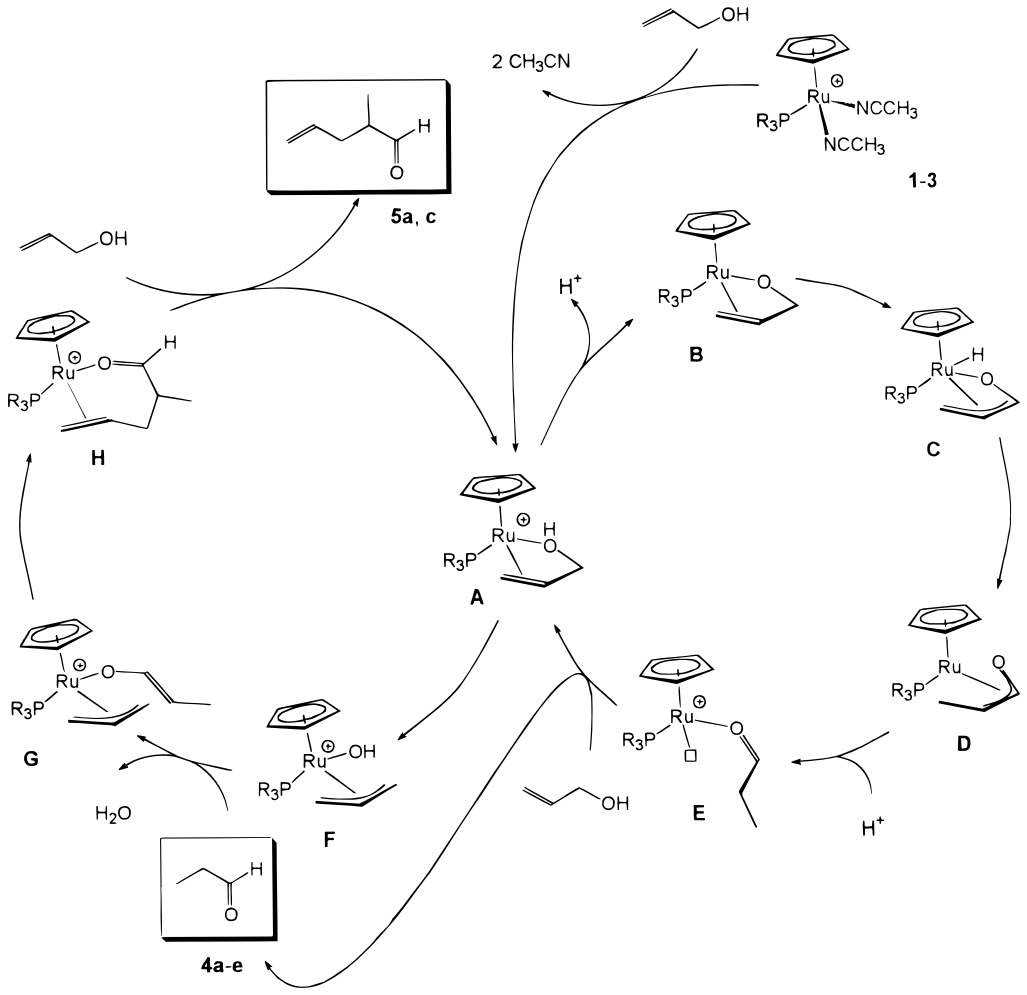

Table 2. Reaction of Allyl Alcohols with 1 and 3 under Optimized Conditions

catalyst (amt, mol %)	*t*, min	*T*, °C	allyl alcohol	product	yield, %	TON	TOF, h^{-1}
1 (0.03)	5	80	R_1 = H	**4a**	60	1800	21500
1 (0.03)	5	75	R_1 = Me	**4b**	85	2570	30800
3 (0.06)	5	110	R_1 = 4-MeC_6H_4	**4c**	94	1660	20000
1 (0.12)	25	110	R_2 = Ph	**4d**	95	760	1815
3 (0.15)	8	57	R_1 = *n*-Hex	**4e**	96	650	7800

frequency (TOF) for the generation of propanal is found to be 1800 and 21 500 h^{-1}, respectively (or 3000 and 36 000 h^{-1}, if quantitative consumption of 2-propenol is taken into account). For comparison, $RuCp(PPh_3)_2Cl$ (0.02 mol %)/NH_4PF_6 (0.8 mol %) at 60 °C gives only low yields of the two allyl acetals of propanal.[1a]

The product distribution was affected by the nature of the phosphine ligand. Thus, the reaction of 1-(4-methylphenyl)-2-propenol with **1** at 57 °C yields predominantly **5c** (72%), whereas with **2** and **3** the reaction pattern is reversed, affording **4c** as the major product in 60 and 67% yields, respectively. This difference in the product distribution may be largely due to electronic reasons. Note that the nucleophilicity of the phosphines increases in the order PPh_3 (2.73) < PMe_3 (8.65) < PCy_3 (9.70), (with the pK_a[4] of the conjugate acid in parentheses), while the bulkiness of the phosphines, as expressed by their cone angles,[5] is increased in the order PMe_3 (118°) < PPh_3 (145°) < PCy_3 (170°). The steric effects of the phosphine ligands in **1**−**3** are most obvious in the redox isomerization of 3-phenyl-2-propenol. On the other hand, with **1** and **2** the corresponding aldehydes are formed in high yields; with **3** no reaction takes place even after prolonged heating.

It should also be noted that the product distribution is sensitive to temperature. Thus, at 110 °C, the reaction of 1-(4-methylphenyl)-2-propenol with **3** (0.06 mol %) quantitatively yields **4c** with no evidence of **5c**. Likewise, with 3-phenyl-2-propenol (Table 1, entries 10−12) no byproducts are observed, and the reaction times are drastically reduced (e.g., catalyst **1**, 0.12 mol %, 25 min, TON = 760, TOF = 1815 h^{-1}; for comparison with $RuCp(PPh_3)_2Cl$ under similar conditions TON = 20, TOF = 2.5 h^{-1}).

The reactions of some allyl alcohols with **1** and **3** under optimized conditions are characterized in Table

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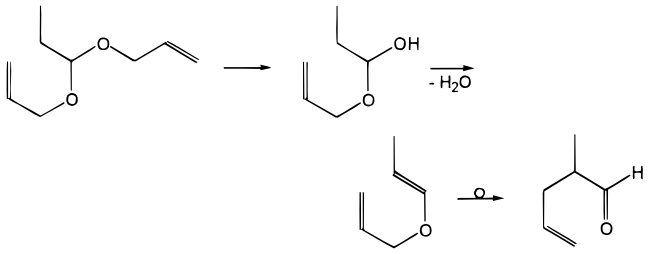
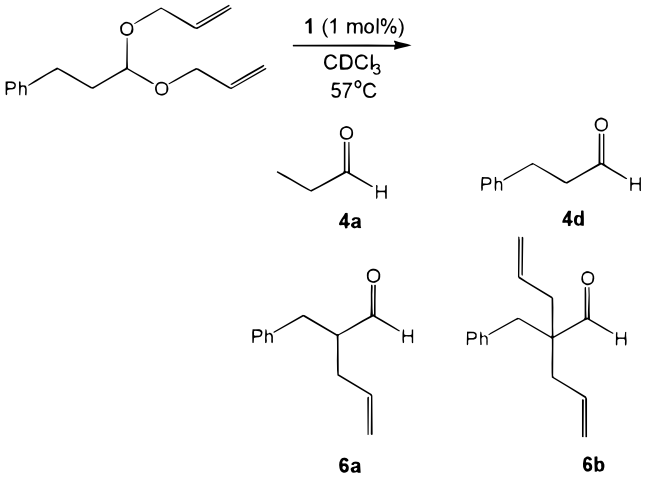
Scheme 2



Scheme 3



2. The mechanistic rationale for the redox isomerization, given recently,[1] is in line with the present observations (Scheme 1). However, the formation of the coupling products **5** needs an additional pathway, likely involving a Claisen rearrangement of the intermediate diallyl acetal of propanal (Scheme 2). In fact, such a reaction is known to proceed at 140 °C with H_3PO_4 as a catalyst.[6] To get evidence for or against this pathway, propanal diallyl acetal has been treated with **1**−**3** in $CDCl_3$ at ∼57 °C. Complete conversion took place after 2 h, resulting in a mixture of propanal (**4a**), 2-methyl-1-pent-4-enal (**5a**), and polymeric aldehydes in a 49:15:34 ratio. Similarly, with 3-phenylpropanal diallyl acetal, under the same reaction conditions but after prolonged reaction times (20 h), a mixture of propanal (**4a**), 3-phenylpropanal (**4d**), 5-phenyl-1-penten-3-al (**6a**), 3-(2-propenyl)-5-phenyl-1-penten-3-al (**6b**), and polymeric aldehydes in a 36:32:6:6:20 ratio was obtained (Scheme 3). These results, especially the formation of **4d** and **6b**, clearly demonstrate that a Claisen rearrangement is not the major pathway. Alternatively, we propose an oxidative addition of the C−O bond giving the ruthenium(IV) allyl−hydroxy species **F**, competing with the β-elimination necessary for the redox isomerization process leading to intermediate **C** (Scheme 3). Worthy of note is the fact that Grotjahn et al. have shown that the related complex $[RuCp(\eta^1(P)\text{-}2\text{-}(PPh_2)\{C_6H_4CH_2(OR)_2\})(CH_3CN)_2]CF_3SO_3$ (R = Me, Et) undergoes an intramolecular oxidative addition of the C−O bond of the dialkyl acetal.[7] A similar C−O activation has been also observed in the Arbuzov rearrangement of allyloxyphosphines.[8]

The next step, then, is the transformation of the incoming aldehyde to give the coordinated enol **G**. Finally, the coupling between enol and allyl results in the formation of **H**, from which the coupled aldehyde is liberated by another allyl alcohol. This mechanism is supported by ruthenium-mediated allylation reactions of carbonyl compounds by allyl acetates and allyl carbonates.[9]

In summary, we have shown that the complexes **1**−**3** (which are readily accessible in 42% overall yield from $RuCl_3 \cdot 3H_2O$ (cf. 90−95% for $RuCp(PPh_3)_2Cl$[10] and 63% for the related indenyl complex $RuInd(PPh_3)_2Cl$[11]) are highly reactive catalysts for the isomerization of allyl alcohols to give carbonyl compounds under relatively mild conditions. Unfortunately, these catalysts also tolerate only a limited substitution pattern on the substrates.

Experimental Section

General Information. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and were used without further purification. The solvents were purified according to standard procedures.[12] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. TLC was performed on Riedel-deHaen TLC sheets (silica gel 60 F 254; layer thickness 0.2 mm). For column chromatography silica gel purchased from Merck (grade 60, 70−230 mesh, 60 Å) was used. $[Ru(Cp)(L)(CH_3CN)_2]PF_6$ (L = PMe_3 (**1**), PPh_3 (**2**), PCy_3 (**3**)) was prepared according to the literature.[2] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$. Compounds were identified by comparison with published NMR data (Aldrich spectra catalog) unless otherwise stated.

NMR Tube Experiments. Typically, a 5 mm NMR tube was charged with a solution of the respective allyl alcohol or acetal in $CDCl_3$ (0.5 mL) together with catalytic amounts of **1**, **2**, or **3** (1 mol %). The NMR tube was capped with a septum and heated at 57 °C. The sample was then transferred to an NMR probe, and ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded.

2-Propenol. A mixture of propanal (**4a**), 2-methyl-1-pent-4-enal (**5a**), and polymeric aldehyde was formed. **4a**: ^1H NMR (δ, $CDCl_3$, 20 °C) 9.70 (t, $^3J_{HH}$ = 1.7 Hz, 1H, CH_3CH_2CHO), 2.36 (dq, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 1.7 Hz, 2H, CH_3CH_2CHO), 1.03 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_3CH_2CHO); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C) 203.5 (CH_3CH_2CHO), 37.7 (CH_3CH_2CHO), 6.5 (CH_3CH_2CHO). Spectroscopic data for **5a** were taken from a mixture of both products: ^1H NMR (δ, $CDCl_3$, 20 °C) 9.61 (d, $^3J_{HH}$ = 1.3 Hz, 1H, CHO), 5.72 (m, 1H, $CH_2{=}CH{-}$), 5.08−4.99 (m, 2H, $CH_2{=}CH{-}$), 2.43 (m, 1H, CHMe), 2.11 (m, 2H, CH_2), 1.05 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C) 205.1 (CHO), 135.5 ($CH_2{=}CH$-), 117.7 ($CH_2{=}CH{-}$), 46.3 (CHMe), 35.3 (CH_2), 13.5 (CH_3).

1-(4-Methylphenyl)-2-propenol. A mixture of 1-(4-methylphenyl)propanone (**4c**) and 1,3-bis(4-methylphenyl)-2-methylpent-4-enone (**5c**) was obtained. **4c** and **5c** were separated by column chromatography (silica gel, CH_2Cl_2 as eluent): **4c**:

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$R_f(CH_2Cl_2)$ = 0.63; ^{1}H NMR (δ, $CDCl_3$, 20 °C) 7.89 (d, 2H, $Ph^{2,6}$), 7.27 (d, 2H, $Ph^{3,5}$), 3.01 (q, 2H, J = 7.3 Hz, CH_2CH_3), 2.44 (s, 3H, CH_3), 1.25 (t, 3H, J = 7.3 Hz, CH_2CH_3).; $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C) 201.2 (1C, *C*O), 144.3 (1C, Ph^4), 135.1 (1C, Ph^1), 129.9 (2C, $Ph^{3,5}$), 128.8 (2C, $Ph^{2,6}$), 32.3 (1C, CH_2-CH_3), 22.3 (1C, H_3C), 9.0 (1C, CH_2CH_3). **5c**: $R_f(CH_2Cl_2)$ = 0.75; the two enantiomeric pairs of diastereomers (ratio: 1.3:1) could not be separated (ma = major isomer, mn = minor isomer); ^{1}H NMR (δ, $CDCl_3$, 20 °C) 7.98 (d, 2H, CO−$Ph^{2,6ma}$), 7.82 (d, 2H, CO−$Ph^{2,6mn}$), 7.36−7.04 (m, 8H, CO−$Ph^{3,5mn}$, CO−$Ph^{3,5mn}$, Ph^{2-6mn}, Ph^{2-6mn}), 6.13−5.94 (m, 2H, H^{4mn}, H^{4ma}), 5.21−4.94 (m, 4H, H^{5mn}, H^{5ma}), 4.03−3.78 (m, 4H, H^{2mn}, H^{2ma}, H^{3mn}, H^{3ma}), 2.48, 2.42, 2.40, 2.27 (s, 12H, Ph−Me), 1.31 (d, 3H, CH−CH_3^{ma}), 1.04 (d, 3H, CH−CH_3^{mn}); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C) 204.0, 203.5 (2C, C^{1ma}, C^{1mn}), 144.4, 144.1, 140.8, 140.6, 140.0, 139.3, 136.7, 136.3, 135.4, 135.0, 130.0, 129.96, 129.9, 129.8, 129.76, 129.1, 129.0, 128.9, 128.8, 128.1 (26C, Ph, C,^{5ma} C^{5mn}), 116.9, 115.8 (2C, C^{4ma}, C^{4mn}), 53.2, 53.0 (2C, C^{2ma}, C^{2mn}), 45.5, 45.4 (2C, C^{3ma}, C^{3mn}), 22.2, 22.1, 21.7, 21.5 (4C, Ph−Me), 17.6, 17.2 (2C, CH−CMe_3^{ma}, CH−CMe_3^{mn}).

3-Phenyl-2-propenol. Predominantly 3-phenylpropanal (**4d**) and traces of intractable byproducts were formed. **4d** was purified by column chromatography (silica gel, CH_2Cl_2 as eluent collecting the band at R_f = 0.56). In the case of catalyst **3**, no reaction took place.

Propanal Diallyl Acetal with 1. All reactions with acetals have been performed by following the protocol above for allyl alcohols. A mixture of propanal (**4a**), 2-methyl-1-pent-4-enal (**5a**), and polymeric aldehydes was formd in a 49:15:34 ratio with complete conversion after 2 h.

3-Phenylpropanal Diallyl Acetal with 1. A mixture of propanal (**4a**), 3-phenylpropanal (**4d**), 5-phenyl-1-penten-3-al (**6a**), 3-(2-propenyl)-5-phenyl-1-penten-3-al (**6b**), and polymeric aldehydes were formed in a 36:32:6:6:20 ratio with complete conversion after 20 h. **6a** and **6b** were separated by column chromatography (silica gel, *n*-hexane/Et_2O (v/v) 3/1 as eluent) **6a**: R_f (*n*-hexane/Et_2O (v/v) 3/1) = 0.81. NMR spectra of **6a** are in agreement with literature reported values.[13] **6b**: R_f (*n*-hexane/Et_2O (v/v) 3/1) = 0.65); ^{1}H NMR (δ, $CDCl_3$, 20 °C) 9.67 (s, 1H, C*H*O), 7.24−7.09 (m, 5H, Ph), 5.91−5.72 (m, 2H, CH_2−CH=CH_2), 5.25−5.06 (m, 4H, CH_2−CH=CH_2), 2.93 (s, 2H, PhCH_2CH), 2.35−2.16 (m, 4H, CH_2−CH=CH_2); $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C) 206.5 (*C*HO), 139.3 (1C, Ph^1), 137.5 (2C, CH_2=*C*HCH_2), 129.0 (2C, $Ph^{2,6}$), 128.9 (2C, $Ph^{3,5}$), 127.3 (Ph^4), 119.7 (2C, *C*H_2=CHCH_2), 53.6 (1C, PhCH_2*C*H), 40.2 (1C, Ph*C*H_2CH), 35.1 (2C, CH_2=CH*C*H_2).

Synthesis. Propanal (4a). A 100 mL flask equipped with a condenser was charged with **3** (30 mg, 44.5 μmol) and 2-propenol (9 mL, 132 mmol) and heated at 80 °C (bath temperature) for 10 min. Propanal was removed by distillation (bp 47 °C). Yield: 4.63 g (60%). The residue of the distillation (3.00 g) contained polymeric propanal. There was no evidence for the formation of **5a**, 2-propenol, or semiacetals or acetals of 2-propenol and propanal.

Butanone (4b). A Schlenk tube charged with neat 3-buten-2-ol (2 mL, 23.07 mmol) and **1** (5 mg, 7.6 μmol) was heated at 75 °C. The reaction was complete after 5 min to give **4b**, which was purified by distillation (bp 80 °C). Yield: 1.41 g (85%). ^{1}H NMR (δ, $CDCl_3$, 20 °C): 2.31 (q, 2H, CH_2CH_3), 1.99 (s, 3H, CO−C*H*$_3$), 0.93 (t, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 209.9 (H_3C−*C*O), 37.1 (*C*H_2CH_3), 29.7 (H_3C−CO), 8.1 (CH_2CH_3).

1-(4-Methylphenyl)propanone (4c). A Schlenk tube charged with a solution of **3** (5 mg, 7.6 μmol) and 1-(4-methylphenyl)-2-propenol (2 mL, 13.46 mmol) in toluene (2.0 mL) was heated at 110 °C. The reaction was monitored by TLC, indicating complete conversion after 5 min to give **4c**. The catalyst was removed by flash chromatography (silica gel, CH_2Cl_2). Yield: 1.88 g (94%). ^{1}H and $^{13}C\{^1H\}$ NMR spectra are in agreement with literature reported values.[14]

3-Phenylpropanal (4d). A Schlenk tube, charged with a solution of **1** (30 mg, 45.8 μmol) and 3-phenyl-2-propenol (5.00 g, 37.26 mmol) in toluene (3.0 mL), was heated at 110 °C. The reaction was monitored by TLC, indicating complete conversion after 25 min to give **4d** exclusively. The catalyst was removed by flash chromatography (silica gel, CH_2Cl_2). Yield: 4.65 g (95%). ^{1}H and $^{13}C\{^1H\}$ NMR spectra are in agreement with literature reported values.[15]

3-Nonanone (4e). A Schlenk tube, charged with a solution of **3** (20 mg, 29.7 μmol) and 1-nonen-3-ol (3.00 g, 19.29 mmol) in $CHCl_3$ (3.0 mL), was heated at 57 °C. The reaction was monitored by TLC, indicating complete conversion after 8 min to give **4e** exclusively. The catalyst was removed by flash chromatography (silica gel, CH_2Cl_2). Yield: 2.88 g (96%). ^{1}H and $^{13}C\{^1H\}$ NMR spectra are in agreement with literature reported values.[16]

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