Synthetic Scope of Ru(OH)$_x$/Al$_2$O$_3$-Catalyzed Hydrogen-Transfer Reactions: An Application to Reduction of Allylic Alcohols by a Sequential Process of Isomerization/Meerwein–Ponndorf–Verley-Type Reduction

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Abstract: Reduction of allylic alcohols can be promoted efficiently by the supported ruthenium catalyst Ru(OH)$_x$/Al$_2$O$_3$. Various allylic alcohols were converted to saturated alcohols in excellent yields by using 2-propanol without any additives. This Ru(OH)$_x$/Al$_2$O$_3$-catalyzed reduction of a dienol proceeds only at the allylic double bond to afford the corresponding enol, and chemoselective isomerization and reduction can be realized under similar conditions. The catalysis is truly heterogeneous and the high catalytic performance can be maintained during at least three recycles of the Ru(OH)$_x$/Al$_2$O$_3$ catalyst. The transformation of allylic alcohols to saturated alcohols consists of three sequential reactions: oxidation of allylic alcohols to α,β-unsaturated carbonyl compounds; reduction of α,β-unsaturated carbonyl compounds to saturated carbonyl compounds; and reduction of saturated carbonyl compounds to saturated alcohols.

Keywords: allylic compounds · heterogeneous catalysis · reaction mechanisms · reduction · ruthenium

Introduction

Reduction of carbon–carbon double bonds is of great importance; classically it has been carried out in the presence of (supported) metal catalysts, including palladium, platinum, ruthenium, rhodium, and nickel. They can activate molecular hydrogen under mild conditions and the reduction is essentially selective and quantitative in the absence of other functional groups.[1] In fine chemical syntheses, the target molecules often have many functional groups such as phenyl, hydroxyl, and alkene, and are susceptible to reduction. For example, selective reduction of allylic alcohols[2] in the presence of other alkenic units is difficult with these metal catalysts. When 5,9-dimethyl-1,8-decadien-3-ol was re-

duced with molecular hydrogen in the presence of the most widely used catalysts, Pd/C or PtO$_2$ (Adam's catalyst),[3] the corresponding saturated alcohol was obtained as a main product (see Scheme S1 in the Supporting Information).[4] Reduction of the remote alkenic bond proceeded nonselectively and therefore the selectivity toward the allylic double bonds with the other alkenic units was poor.

Very recently, Cadierno and co-workers have developed the catalytic selective reduction of allylic alcohols with an alcohol as the source of hydrogen.[5] As far as we know, this is the first example of allylic alcohol reduction using such a hydrogen source; similar systems were previously unknown. The advantages of the method in comparison with classical metal catalysts are the high selectivity toward the allylic double bonds without allylic C−O bond cleavage and reduction of remote alkenic bonds. This is because the mechanism is completely different.[5] Although various allylic alcohols can be converted into the corresponding saturated alcohols, the system has shortcomings in a) the recovery and reuse of (expensive) catalysts and b) the indispensability of bases as co-catalysts (a problem of product contamination).

The development of easily recoverable and recyclable heterogeneous catalysts by filtration or centrifugation can solve the problems of the homogeneous systems and has received particular research interest.[6] Although the immobilization of homogeneous catalysts on inert solid supports and attach-

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ment of the catalytically active species through covalent or ionic bonds with (modified) supports has been studied extensively, the intrinsic catalytic activities and selectivities of the homogeneous catalysts are usually much decreased by the heterogenization.[7] Leaching of the heterogeneous catalysts is also responsible for severe drawbacks and is observed in many cases.[7] Therefore, the design of truly efficient heterogeneous catalysts with activities and selectivities comparable with or higher than those of the corresponding homogeneous analogues is one of the most important challenges in modern organic syntheses, especially for fine chemicals.[6]
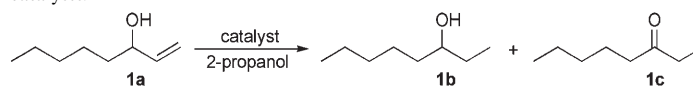
Here, we report that supported ruthenium hydroxide[8] can act as an efficient heterogeneous catalyst for the reduction of allylic alcohols to saturated alcohols with high chemoselectivity using 2-propanol as both the solvent and the hydrogen source. The present system has the following significant advantages: a) applicability to various kinds of allylic alcohols; b) high chemoselectivity toward allylic double bonds in the presence of other alkenic units; c) higher catalytic activity than that of the homogeneous analogue;[5] d) a simple workup procedure, namely catalyst/product separation; e) reusability of the $Ru(OH)_x/Al_2O_3$ catalyst; f) no use of bases as co-catalysts; and g) use of an easily prepared $Ru(OH)_x/Al_2O_3$ catalyst. We also report our investigation of the reaction mechanism for the reduction.

Results and Discussion

Synthetic scope of the $Ru(OH)_x/Al_2O_3$-catalyzed system: First, the catalytic activity and selectivity for the reduction of 1-octen-3-ol (**1a**) to 3-octanol (**1b**) were compared among various catalysts (Table 1). The conversion of **1a** was <1% in the absence of the catalyst, or in the presence of Al_2O_3 or Al_2O_3 treated with an aqueous NaOH solution (entries 18, 19, and 21). A homogeneous base, NaOH, did not catalyze the transformation (entry 20). In the presence of the catalyst precursor $RuCl_3 \cdot nH_2O$, mainly the dehydration products were formed (entry 11). Heterogeneous catalysts such as Ru/C (Ru metal on carbon), Ru–HAP (Ru–Cl species on hydroxyapatite), and RuO_2 (bulk oxide) did not produce the corresponding saturated alcohol **1b** (entries 7–9). Although $[RuCl_2(PPh_3)_3]$ and $[\{RuCl_2(p\text{-cymene})\}_2]$ have been reported to be active for the reduction in the presence of bases such as Cs_2CO_3 (at least 2 equiv with respect to Ru),[5,9] the corresponding saturated alcohol **1b** was not formed in the absence of bases (entries 13 and 15). Complexes $K_4[Ru_2OCl_{10}]$, $[Ru(acac)_3]$, $[RuCp_2]$, and $[Ru_3(CO)_{12}]$ were inactive under the present conditions (entries 10, 12, 16, and 17). Among various ruthenium catalysts tested, only supported ruthenium hydroxide catalysts gave the corresponding saturated alcohol **1b** (entries 1–4). The ruthenium hydroxides supported on high BET surface area Al_2O_3 (160 $m^2 g^{-1}$), TiO_2 (316 $m^2 g^{-1}$), and SiO_2 (273 $m^2 g^{-1}$) exhibited high catalytic activity for the transformation (entries 1–3), whereas the catalytic activity of those on low BET sur-

Table 1. Reduction of 1-octen-3-ol (**1a**) to 3-octanol (**1b**) with various catalysts.[a]

Entry	Catalyst	Conv. of **1a** [%][b]	Yield [%][b]	
			1b	**1c**
1	$Ru(OH)_x/Al_2O_3$	>99	94	6
2	$Ru(OH)_x/TiO_2$	>99	94	6
3	$Ru(OH)_x/SiO_2$	>99	81	19
4	$Ru(OH)_x/Fe_3O_4$	>99	13	87
5	$Ru(OH)_x/ZnO$	69	nd	69
6	$RuCl_x/Al_2O_3$[c]	>99	12	88
7	Ru/C	3	nd	1
8	Ru–HAP	1	nd	1
9	RuO_2 (anhydrous)	<1	nd	nd
10	$K_4[Ru_2OCl_{10}]$	41	nd	5
11	$RuCl_3 \cdot nH_2O$	96	nd	21[d]
12	$[Ru(acac)_3]$	3	nd	3
13	$[RuCl_2(PPh_3)_3]$	>99	nd	95
14	$[RuCl_2(bpy)_2]$	<1	nd	nd
15	$[\{RuCl_2(p\text{-cymene})\}_2]$	3	nd	3
16	$[RuCp_2]$	3	nd	3
17	$[Ru_3(CO)_{12}]$	11	nd	10
18[e]	Al_2O_3	<1	nd	nd
19[e]	Al_2O_3[f]	<1	nd	nd
20[g]	NaOH	<1	nd	nd
21	none	<1	nd	nd
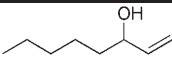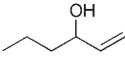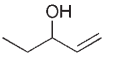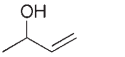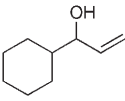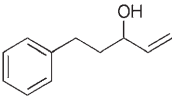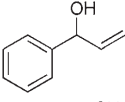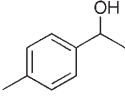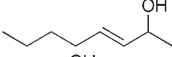
[a] Reaction conditions: **1a** (1 mmol), catalyst (Ru: 2 mol%), 2-propanol (3 mL), 363 K (bath temp.), 2 h, under 1 atm Ar. [b] Determined by GC using an internal standard technique; nd = not detected. [c] Prepared without base pretreatment. [d] The main by-product was 1,3-octadiene. [e] 82 mg. [f] Treated with an aqueous NaOH solution (pH 13). [g] 2 mol%.

face area Fe_3O_4 (6.8 $m^2 g^{-1}$) and ZnO (2.9 $m^2 g^{-1}$) was much lower.[10] The pretreatment of the catalysts with a base increased the activity significantly (entry 1 versus entry 6). This is probably because of the generation of the active ruthenium hydroxide species on the surface of supports, according to the report that the ruthenium alkoxide complexes, which are the true active spec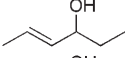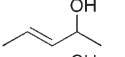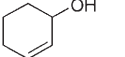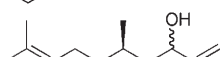ies for the isomerization of allylic alcohols, are generated by the reaction of ruthenium halide complexes with KOtBu.[9a]

To verify whether the observed catalysis is derived from solid $Ru(OH)_x/Al_2O_3$ or leached ruthenium species, after reduction of **1a** under the conditions in Table 1 and filtration of the $Ru(OH)_x/Al_2O_3$ catalyst from the reaction mixture at the reaction temperature, the reaction was performed again under the same conditions with the filtrate. It was completely stopped by removal of the catalyst. Moreover, ICP-AES analysis confirmed that no ruthenium was detected in the filtrate (Ru content below the 7 ppb detection limit). These facts can rule out any contribution from ruthenium species that leached into the reaction solution to the observed catalysis, which is intrinsically heterogeneous.[11]
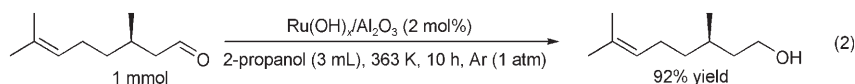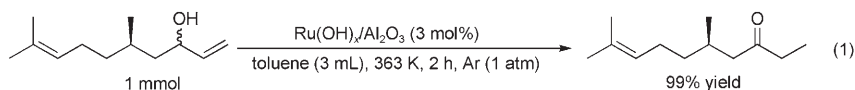
The scope of the present $Ru(OH)_x/Al_2O_3$-catalyzed system with regard to various structurally diverse allylic alcohols was examined. The $Ru(OH)_x/Al_2O_3$ catalyst showed high catalytic activities for terminal, internal, and cyclic allylic alcohols, as summarized in Table 2. Terminal aliphatic

Table 2. Reduction of various allylic alcohols to saturated alcohols catalyzed by Ru(OH)$_x$/Al$_2$O$_3$.[a]

Entry	Substrate		Ru [mol%]	t [h]	Conv. [%][b]	Yield [%][b]
1		**1a**	2	2	>99	94
2[c]	**1a**, 1st reuse		2	2	>99	95
3[c]	**1a**, 2nd reuse		2	2	>99	95
4[c]	**1a**, 3rd reuse		2	2	>99	95
5		**2a**	2	0.5	>99	94
6		**3a**	2	0.5	>99	96
7		**4a**	2	0.5	>99	97
8		**5a**	2	3	>99	90
9[d]		**6a**	5	10	>99	82
10[d]		**7a**	5	2	>99	85
11[d]		**8a**	5	4.5	>99	83
12		**9a**	5	1	>99	94
13		**10a**	5	3	>99	93
14		**11a**	5	3	>99	95
15		**12a**	3	1.5	>99	98
16[e]		**13a**	3	5	>99	91

[a] Reaction conditions: substrate (1 mmol), Ru(OH)$_x$/Al$_2$O$_3$ (Ru: 2–5 mol%), 2-propanol (3 mL), 363 K (bath temp.), under 1 atm Ar. [b] Determined by GC using an internal standard technique. The main by-products were the corresponding saturated ketones. [c] Recycling experiment: the reaction conditions were the same as those for the first run with a fresh catalyst. The reaction rate for the recycling experiment was almost the same as that for the first run with the fresh catalyst. [d] 393 K (bath temp.). [e] Reaction conditions: i) substrate (1 mmol), Ru(OH)$_x$/Al$_2$O$_3$ (Ru: 3 mol%), toluene (3 mL), 363 K (bath temp.), 2 h, under 1 atm Ar, ii) followed by addition of 2-propanol (1 mL), 363 K (bath temp.), 3 h, under 1 atm Ar.
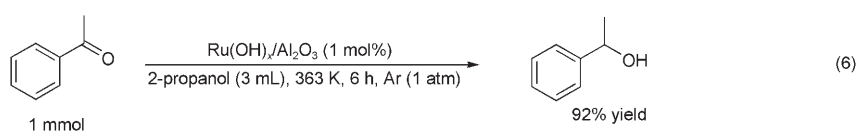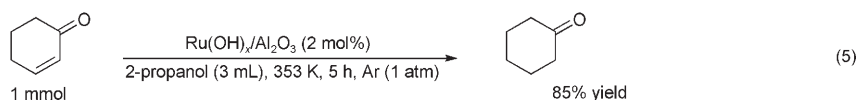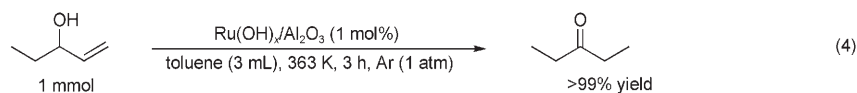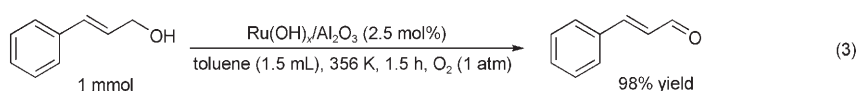
the previously reported homogeneous [{RuCl$_2$(η^6-C$_6$Me$_6$)}$_2$]/Cs$_2$CO$_3$ system (TOF = 28 h^{-1}).[5] The reduction of benzylic β,γ-unsaturated alcohols (**7a** and **8a**) proceeded efficiently to afford the corresponding benzylic alcohols without reduction of the aromatic rings (entries 10 and 11). Not only terminal allylic alcohols but also internal ones (**9a**–**12a**) could be reduced to the corresponding saturated alcohols in high yields (entries 12–15). Reduction of dienol **13a** proceeded only at the allylic double bonds to afford the corresponding enol (entry 16). Furthermore, chemoselective isomerization [Eq. (1)] and reduction [Eq. (2)] could be realized under similar conditions.

The present transformation of allylic alcohols to saturated alcohols consists of three sequential reactions: oxidation of allylic alcohols to α,β-unsaturated carbonyl compounds; reduction of α,β-unsaturated carbonyl compounds to saturated ones; and reduction of saturated carbonyl compounds to saturated alcohols (see the next section). In the presence of Ru(OH)$_x$/Al$_2$O$_3$, various functional transformations such as a) oxidation of α,β-unsaturated alcohols [Eq. (3)], isomerization of α,β-unsaturated alcohols [Eqs. (1)

allylic alcohols (**1a**–**6a**), especially, were converted to the corresponding saturated alcohols in high yields (entries 1–9). The recovered Ru(OH)$_x$/Al$_2$O$_3$ catalyst after the reduction of **1a** could be recycled at least three times without appreciable loss of the original catalytic activity (entries 2–4). The Ru(OH)$_x$/Al$_2$O$_3$-catalyzed reduction rate increased with increasing reaction temperature (up to 393 K), and the turnover frequency (TOF) for the reduction of **1a** reached up to 110 h^{-1} at 393 K (bath temperature) with maintenance of the high selectivity (92%). The TOF was higher than that of

and (4)], reduction of α,β-unsaturated ketones [Eq. (5)], and Meerwein–Ponndorf–Verley-type (MPV-type) reduction [Eq. (6)] could be realized as shown. Thus, this system has wide applicability.

$$\text{(3)}$$

Ru(OH)$_x$/Al$_2$O$_3$ (2.5 mol%), toluene (1.5 mL), 356 K, 1.5 h, O$_2$ (1 atm)

1 mmol → 98% yield

$$\text{(4)}$$

Ru(OH)$_x$/Al$_2$O$_3$ (1 mol%), toluene (3 mL), 363 K, 3 h, Ar (1 atm)

1 mmol → >99% yield

$$\text{(5)}$$

Ru(OH)$_x$/Al$_2$O$_3$ (2 mol%), 2-propanol (3 mL), 353 K, 5 h, Ar (1 atm)

1 mmol → 85% yield

$$\text{(6)}$$

Ru(OH)$_x$/Al$_2$O$_3$ (1 mol%), 2-propanol (3 mL), 363 K, 6 h, Ar (1 atm)

1 mmol → 92% yield

hydrogen is relocated to the 1-carbon atoms in the first isomerization step.[8c,9b,g] When **1a** was reduced in 2-deuterio-2-propanol, 3-deuterio-3-octanol was obtained as a main product (entry 3) and the α-deuterium of 2-deuterio-2-propanol was transferred to the 3-carbon atom. In addition, the transformation of **14a** in 2-deuterio-2-propanol gave 1,3-dideuterio-3-octanol as a main product (entry 4). These results show that the α-hydrogen of 2-propanol is transferred to the 3-carbon atom in the product.

It is likely that the ruthenium hydride is a key species in both

Mechanistic studies: The reduction of the homoallylic alcohol 4-phenyl-1-buten-4-ol and the allylic acetate ester 3-acetoxy-1-octene hardly occurred under the present conditions. Therefore, the substrates need both an allylic hydroxyl group and a double bond for this reduction. The reaction profiles for the reduction of **1a** to **1b** showed that the saturated ketone **1c** was formed initially, followed by **1b**, suggesting that the transformation proceeds by sequential reactions, that is, isomerization of α,β-unsaturated alcohols to saturated carbonyl compounds followed by MPV-type reduction to the corresponding saturated alcohols.[5]
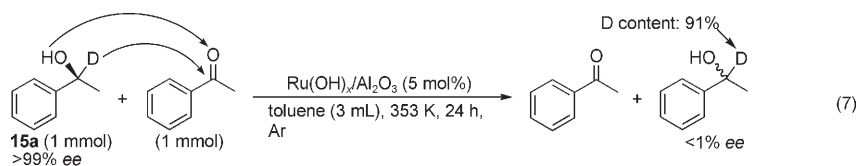
In deuterium labeling experiments to investigate the reaction mechanism (Table 3), the reduction of a monodeuterated allylic alcohol 3-deuterio-1-octen-3-ol (**14a**) in 2-propanol gave the corresponding saturated alcohol in 95% yield. The deuterium was observed mainly at the 1-position (content 20%) of the product and hardly at the 2- and 3-positions (entry 1), showing that 60% of the α-deuterium in **14a** was transferred to the 1-position. In toluene in the absence of 2-propanol, 1-deuterio-3-octanone was obtained in 98% yield (entry 2) and the α-deuterium of **14a** was transferred quantitatively to the 1-position. Therefore, the Ru(OH)$_x$/Al$_2$O$_3$ catalyst can distinguish the α-hydrogen from the hydrogen in the hydroxyl group, and the α-

Table 3. Deuterium (D) labeling experiments for the reduction of 1-octen-3-ol (**1a** and **14a**).[a]

| Entry	Substrate		Solvent	t [h]	Yield [%][b]	D content [%][c]		
						1-position	2-position	3-position
1	HO D (structure)	**14a**	HO H (structure)	2	95	20	<1	2
2[d]	HO D (structure)	**14a**	(toluene structure)	12	98[e]	33	<1	–
3	HO H (structure)	**1a**	HO D (structure)	24	93	1	<1	84
4	HO D (structure)	**14a**	HO D (structure)	24	95	32	<1	86

[a] Reaction conditions: substrate (1 mmol), Ru(OH)$_x$/Al$_2$O$_3$ (Ru: 2 mol%), solvent (3 mL), 363 K (bath temp.), under 1 atm Ar. [b] Determined by GC using an internal standard technique. [c] Determined by ^{2}H NMR. [d] Ru: 5 mol%. [e] 1-Deuterio-3-octanone was formed as sole product.

the isomerization and the MPV-type reduction.[9] Therefore, the hydrogen transfer racemization of (S)-1-deuterio-1-phenylethanol (**15a**) in the presence of a hydrogen acceptor (acetophenone) under similar conditions was carried out according to Bäckvall's procedures to clarify the nature of the hydride species.[12] The deuterium content at the α-position of the corresponding racemic alcohol was high (91%) after complete racemization [Eq. (7)], suggesting formation of the ruthenium monohydride species on Ru(OH)$_x$/Al$_2$O$_3$.[12]

$$\text{(7)}$$

Ru(OH)$_x$/Al$_2$O$_3$ (5 mol%), toluene (3 mL), 353 K, 24 h, Ar

15a (1 mmol) >99% ee + (1 mmol) → D content: 91%, <1% ee

On the basis of the above results, we propose a possible reaction mechanism for the present Ru(OH)$_x$/Al$_2$O$_3$-catalyzed reduction of allylic alcohols (Scheme 1). Initially, the catalyt-
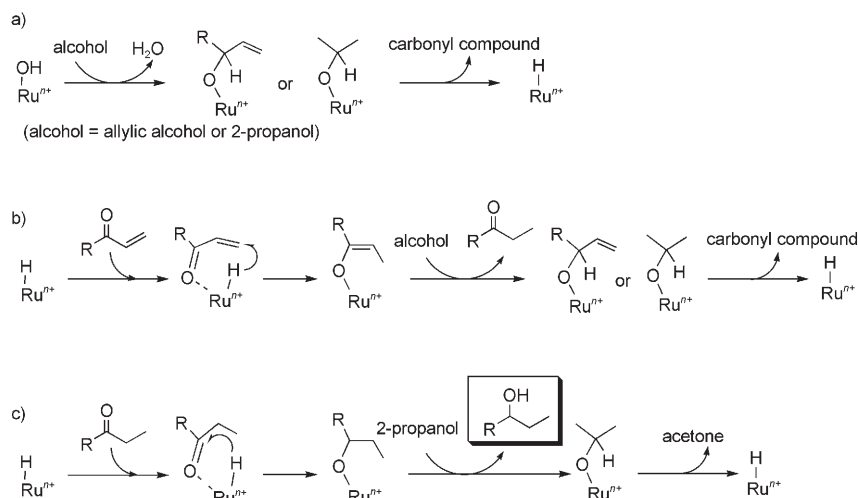
Scheme 1. A possible reaction mechanism for Ru(OH)$_x$/Al$_2$O$_3$-catalyzed reduction of allylic alcohols in the presence of 2-propanol.

ically active ruthenium monohydride species is formed by the reaction of ruthenium hydroxide species with an alcohol (allylic alcohol or 2-propanol) (Scheme 1a).[8] The 1,4-addition of the hydride species to the α,β-unsaturated carbonyl compound[13] formed by the reaction of the ruthenium hydroxide species with an allylic alcohol yielding the σ-enolate species is followed by intermolecular ligand exchange with an alcohol (allylic alcohol or 2-propanol) to give the corresponding saturated carbonyl compound as an intermediate (Scheme 1b).[9a, 14] Then the MPV-type reduction of the intermediate carbonyl compound proceeds to give the corresponding saturated alcohol (Scheme 1c). It was confirmed that Al$_2$O$_3$ and Al$_2$O$_3$ treated with an aqueous NaOH solution do not catalyze the MPV-type reduction of **1c** under the present conditions, suggesting that the catalytic activity for the MPV-type reduction originates from ruthenium species.[15]

Whereas the formation rate of the final saturated alcohol in the reduction of **1a** in 2-deuterio-2-propanol was much lower than that in 2-propanol (entry 1 in Table 1 versus entry 3 in Table 3), the rate of the initial isomerization step in 2-deuterio-2-propanol ($R = 22.6$ mM min^{-1}) was fairly similar to that in 2-propanol (26.1 mM min^{-1}). This suggests that the MPV-type reduction (Scheme 1c) is the rate-determining step for this transformation.[16]

Conclusion

Ru(OH)$_x$/Al$_2$O$_3$ can act as a heterogeneous catalyst for the reduction of allylic alcohols. Thus various terminal and internal allylic alcohols can be converted to the corresponding saturated alcohols. Furthermore, the catalyst/product separation can easily be carried out and the Ru(OH)$_x$/Al$_2$O$_3$ is recyclable.

Experimental Section

General: NMR spectra were recorded on a JEOL JNM-EX-270 instrument. ^{1}H and ^{13}C NMR spectra were measured at 270 and 67.8 MHz, respectively, in [D$_1$]chloroform with TMS as an internal standard. ^{2}H NMR spectra were measured at 41.25 MHz using [D$_6$]benzene as an external standard. GC analyses were performed on a Shimadzu GC-2014 instrument using a flame ionization detector equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). Mass spectra were recorded on a Shimadzu GCMS-QP2010 equipped with a TC-5HT capillary column (internal diameter = 0.25 mm, length = 30 m). Reagents and substrates (except for **5a–8a** and **13a–15a**) were obtained commercially from Tokyo Kasei, Aldrich, and Fluka (reagent grade) and used without further purification. 2-Propanol (Kanto) and 2-deuterio-2-propanol (Cambridge Isotope Laboratory) were particularly carefully purified (degassed) before use.[17] Al$_2$O$_3$ (KHS-24, BET surface area 160 m^{2}g^{-1}), TiO$_2$ (ST-01, 316 m^{2}g^{-1}), SiO$_2$ (CARiACT Q-10, 273 m^{2}g^{-1}), Fe$_3$O$_4$ (Cat. No. 310069, 6.8 m^{2}g^{-1}), and ZnO (Cat. No. 37002-95, 2.9 m^{2}g^{-1}) were obtained from Sumitomo Chemical, Ishihara Sangyo Kaisya, Fuji Silysia, Aldrich, and Nacalai Tesque, respectively. Supported metal catalysts (5 wt%) were supplied by NE Chemcat. Ru–HAP (ruthenium on HAP, 9.1 wt%) was purchased from Wako. Compounds **5a–8a** and **13a** were synthesized by Grignard reaction of the corresponding aldehydes with vinylmagnesium bromide.[9g] Compound **14a** was synthesized by oxidation of **1a**[18] followed by reduction with lithium aluminum deuteride.[19] Compound **15a** was synthesized according to the literature procedures.[8c, 12] See the Supporting Information for the synthetic procedures for the allylic alcohols **5a–8a**, and **13a** and the deuterated compounds **14a** and **15a**.

Preparation of supported ruthenium hydroxide catalysts: The supported ruthenium hydroxide catalysts were prepared by the procedure reported previously.[8] Al$_2$O$_3$ powder (2.0 g) calcined at 823 K for 3 h was stirred vigorously with an aqueous solution (60 mL) of RuCl$_3$ (8.3 mM) at room temperature. After 15 min, the pH of the solution was adjusted slowly to 13.2 by addition of an aqueous NaOH solution (1.0 M) and the resulting slurry was stirred for 24 h. The solid was filtered off, washed with a large amount of water, and dried in vacuo; yield of Ru(OH)$_x$/Al$_2$O$_3$ 2.1 g (dark green powder, ruthenium content 2.0–2.1 wt%). The XRD pattern of Ru(OH)$_x$/Al$_2$O$_3$ was the same as that of the parent Al$_2$O$_3$ support and no signals from Ru metal (clusters) and RuO$_2$ were observed. Particles of Ru metal (clusters) and RuO$_2$ were not detected by TEM. The binding energies of Ru 3d$_{5/2}$ and Ru 3p$_{3/2}$ of Ru(OH)$_x$/Al$_2$O$_3$ (XPS) were detected at 281.8 (full width at half maximum (FWHM) 2.4 eV) and 463.5 eV (FWHM 4.7 eV), respectively, showing that the oxidation state of the ruthenium species in Ru(OH)$_x$/Al$_2$O$_3$ is +3.[20] The IR spectrum showed a very broad ν(OH) band in the range 3000–3700 cm^{-1}. These facts suggest that ruthenium(III) hydroxide is highly dispersed on Al$_2$O$_3$.

Ru(OH)$_x$/Al$_2$O$_3$-catalyzed reduction: All operations for the reactions were performed in a glove box under Ar. Ru(OH)$_x$/Al$_2$O$_3$ (2 mol% Ru), **1a** (1 mmol), and 2-propanol (3 mL) were placed successively in a Pyrex glass vial. The reaction mixture was stirred vigorously with a Teflon-coated magnetic stir bar (800 rpm) at 363 K (bath temperature) under Ar

(1 atm). The conversion and yield(s) were determined periodically by GC analysis.

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