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Dehydrogenation, hydrogenolysis, isomerization and hydrogenation of 3-phenylprop-2-en-1-ol with carbonylperchloratobis(triphenylphosphine)iridium(I) and carbonyldihydridoperchloratobis(triphenylphosphine)-iridium(III)

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Abstract

Reaction of 3-phenylprop-2-en-1-ol (**1**) with $Ir(ClO_4)(CO)(PPh_3)_2$ (**2**) under nitrogen at 25 °C gives 3-phenylprop-2-enal (**4**), 3-phenylprop-2-ene (**5**), and 3-phenylpropanal (**6**). Dehydrogenation of **1** by **2** gives $Ir(H)_2(ClO_4)(CO)(PPh_3)_2$ (**3**) which reacts with another molecule of **1** to give **5**, **2** and H_2O. Isomerization of **1** to **6** rapidly occurs and hydrogenation of **6** to 3-phenylpropan-1-ol (**12**) slowly follows in the presence of **2** under hydrogen at 25 °C. The catalytically active species for the isomerization under nitrogen seems to be **3**.

Introduction

Metal-catalyzed reactions of alcohols are diverse. Hydroxyl group-directed hydrogenation of unsaturated alcohols to give saturated alcohols has long been of interest in the field of stereoselective organic synthesis [1]. Various isomerizations of unsaturated alcohols, to produce carbonyl compounds have been studied [2]. The dehydrogenation of alcohols has provided valuable information on the production of hydrogen from alcohols [3]. Conversion of alcohols into the correspondng hydrocarbons has been reported and can be utilized in a variety of organic syntheses [4]. Here, we report on the catalytic reactions, dehydrogenation, hydrogenolysis, isomerization, and hydrogenation of 3-phenylprop-2-en-1-ol (**1**) with $Ir(ClO_4)(CO)(PPh_3)_2$ (**2**) and $Ir(H)_2(ClO_4)(CO)(PPh_3)_2$ (**3**) (along with detailed experimental results).

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Results and discussion

Dehydrogenation and hydrogenolysis of 3-phenylprop-2-en-1-ol (1) with $Ir(ClO_4)(CO)(PPh_3)_2$ (2) and $Ir(H)_2(ClO_4)(CO)(PPh_3)_2$ (3)

The reaction of **1** with **2** under different conditions yields dehydrogenation, hydrogenolysis and isomerization products under nitrogen at 25 °C (eq. 1) (see Table 1). The dehydrogenation of alcohols, to give the corresponding carbonyl compounds, is known to be initiated by the formation of alkoxometal species in the presence of base (A^-) which is originally coordinated to the metal [5] or to the

$$\underset{(1)}{C_6H_5CH{=}CHCH_2OH} \xrightarrow[N_2,\,25\,^\circ C]{IR(ClO_4)(CO)(PPh_3)_2\,(2)} \underset{(4)}{C_6H_5CH{=}CHCHO} + \underset{(5)}{C_6H_5CH{=}CHCH_3} + \underset{(6)}{C_6H_5CH_2CH_2CHO} + H_2O \quad (1)$$

non-coordinated anion (eq. 2) [3a,6]. Dehydrogenation may also be initiated by the formation of hydridoalkoxometal species in the absence of base (eq. 3) [3c,4a]. One may expect the dehydrogenation of **1** by **2** to occur via alkoxometal species rather

$$LnM^+ + RR'CHOH \xrightarrow[-HA]{A^-} LnM-OCHRR' \xrightarrow{-RR'CO} LnMH \xrightarrow[-H_2]{HA} LnM^+ + A^- \quad (2)$$

$$LnM + RR'CHOH \rightarrow LnM(H)(-OCHRR') \xrightarrow[-H_2]{} LnM + RR'CO \quad (3)$$

than through hydridoalkoxometal since it is well-known that complex **2** readily releases ClO_4^- ligand in alcohol solution to give the complex, $[Ir(alcohol)(CO)(PPh_3)_2]^+$ [7]. The reactions of **1** with **2**, which yield **4** and **5** however, seem to proceed according to eq. 4 (via hydridoalkoxoiridium(III) (**9**)) and eq. 5 for the following reasons. (1) Addition of ClO_4^- to the reaction mixture actually suppresses the production of **4** (Table 1), which excludes the OH hydrogen abstraction by the ClO_4^- group. (2) The dihydridoiridium(III) complex **3** is very stable [8]. (3) Most of hydrogen abstracted from **1** to yield **4** is used in the production of **5** and H_2O (see

Table 1

Catalytic reactions of 3-phenylprop-2-en-1-ol (**1**) with $Ir(ClO_4)(CO)(PPh_3)_2$ (**2**), $[Ir(CO)(PPh_3)_3]ClO_4$ (**7**) and $[Ir(CO)(PPh_3)_3]BF_4$ (**8**) in $CDCl_3$ under nitrogen for 5 h

Catalyst	Temp. (°C)	Product (%) [a]			Unreacted **1**
		4 [b]	**5** [c]	**6** [d]	
2 [e]	25	40	40	3	17
2 [e,f]	25	34	32	2	32
2 [e,g]	60	40	36	7	17
7 [h]	60	45	43	6	6
8 [h]	60	46	43	6	5

[a] H_2O was also detected in all experiments ($H_2O/5 = 1.0$). [b] $C_6H_5CH{=}CHCHO$. [c] $C_6H_5CH{=}CHCH_3$. [d] $C_6H_5CH_2CH_2CHO$. [e] 6.0 mmol of **1** and 0.2 mmol of **2** were used in 5.0 ml of $CDCl_3$. [f] In $NaClO_4$ saturated solution. [g] Data obtained after 2 h of reaction. [h] 2.0 mmol of **1** and 0.2 mmol of **7** (or **8**) were used in 5.0 ml of $CDCl_3$.

Table 2

Catalytic reactions of 3-phenylprop-2-en-1-ol (**1**) (0.1–1.0 mmol) with $Ir(H)_2(ClO)_4)(CO)(PPh_3)_2$ (**3**) (0.1 mmol) in $CDCl_3$ (2.0 ml) under nitrogen at 25 °C

Mole ratio (1/3)	Product (%) [a]			Time (h) [e]
	4 [b]	5 [c]	6 [d]	
1		36	64	10
2		44	56	13
4	31	53	16	19
10	38	51	11	24

[a] H_2O was also detected in all experiments. [b] $C_6H_5CH{=}CHCHO$. [c] $C_6H_5CH{=}CHCH_3$. [d] $C_6H_5CH_2CH_2CHO$. [e] Elapsed time until all **1** had disappeared.

Table 1). (4) **5** is produced in large amount in the reaction of **3** with **1** (see Table 2) in which no dehydrogenation product (**4**) is formed.

$$\mathbf{1} + \mathbf{2} \rightarrow \underset{(\mathbf{9})}{Ir(H)(OCH_2CH{=}CHC_6H_5)(ClO_4)(CO)(PPh_3)_2} \rightarrow$$

$$\underset{(\mathbf{3})}{Ir(H)_2(ClO_4)(CO)(PPh_3)_2} + \mathbf{4} \quad (4)$$

$$\mathbf{1} + \mathbf{3} \rightarrow \mathbf{2} + \mathbf{5} + H_2O \quad (5)$$

The reactions of $[Ir(CO)(PPh_3)_3]^+$ do furnish some useful information on the dehydrogenation and hydrogenolysis of **1** with **2** on the assumption that $[Ir(CO)(PPh_3)_3]^+$ and **2** follow the similar pathways upon reaction with **1**. The reactions of **1** with $[Ir(CO)(PPh_3)_3]ClO_4$ (**7**) and $[Ir(CO)(PPh_3)_3]BF_4$ (**8**) are much slower than those with **2** (Table 1), to be discussed later. Almost the same results were obtained in the reactions of **1** with **7** and **8** (Table 1), which suggests that the role of the anions ClO_4^- and BF_4^- of the hydroxyl hydrogen abstraction is negligible and that the hydridoalkoxoiridium(III) species ($[Ir(H)(OCH_2CH{=}CH\text{-}C_6H_5)(CO)(PPh_3)_3]^+$) is the intermediate.

An intermolecular hydrogen transfer between alcohol molecules has been suggested for various reactions of alcohols with metal complexs [4a,9–12]. Dehydrogenation and hydrogenolysis of **1** with **2** do not seem to involve direct intermolecular hydrogen transfer between molecules of **1**. The yield of the dehydrogenation product is significantly higher than that of the hydrogenolysis product at high temperature (Table 1). Some of the H_2 generated from **3** (the dehydrogenation product of **1**) is lost presumably by the well-known reductive elimination, $\mathbf{3} \rightarrow \mathbf{2} + H_2$ [8], a reaction which should be significant at elevated temperature.

Reaction of a mixture of **1** and hydroxyl-hydrogen-deuterated 3-phenylprop-2-en-1-ol, $C_6H_5CH{=}CHCH_2OD$ (**1D**) [13*] provided interesting results (eq. 6) in support of eqs. 4 and 5, and is accordingly outlined in eqs. 7 and 8.

* Reference number with asterisk indicates a note in the list of references.

$$\underset{(\mathbf{1D},90\%)}{C_6H_5CH{=}CHCH_2OD} + \underset{(\mathbf{1},10\%)}{C_6H_5CH{=}CHCH_2OH} \xrightarrow[25\,^\circ C,\,5\,h]{\mathbf{2},\,CDCl_3,\,N_2}$$

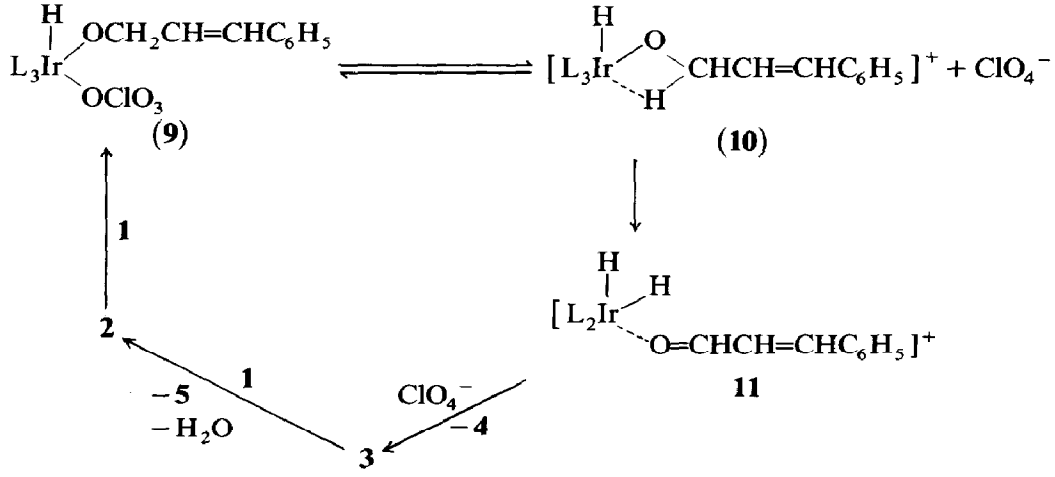
$$\underset{(\mathbf{4},40\%)}{C_6H_5CH{=}CHCHO} + \underset{(\mathbf{5},24\%)}{C_6H_5CH{=}CHCH_3} + \underset{(\mathbf{5D},16\%)}{C_6H_5CH{=}CHCH_2D} +$$

$$\underset{(\mathbf{6},2\%)}{C_6H_5CH_2CH_2CHO} + H_2O + HDO + D_2O \quad (6)$$

$$\underset{(\mathbf{1D})}{C_6H_5CH{=}CHCH_2OD} + \mathbf{2} \rightarrow \underset{(\mathbf{4})}{C_6H_5CH{=}CHCHO} + \underset{(\mathbf{3D})}{Ir(H)(D)(ClO_4)(CO)(PPh_3)_2} \quad (7)$$

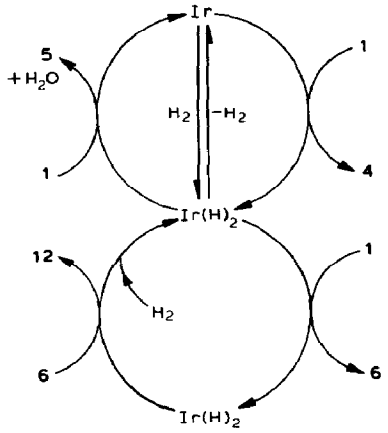
$$\mathbf{1D} + \mathbf{3D} \rightarrow \underset{(\mathbf{5})}{\tfrac{1}{2}C_6H_5CH{=}CHCH_3} + \underset{(\mathbf{5D})}{\tfrac{1}{2}C_6H_5CH{=}CHCH_2D} + \mathbf{2} + \tfrac{1}{2}HDO + \tfrac{1}{2}D_2O \quad (8)$$

The lower yield of products obtained from the reaction of **1** with **2** in the presence of an excess of ClO_4^- (Table 1) can be as proposed in Scheme 1. An excess of ClO_4^- supresses the formation of **10**. The ClO_4^- group in **2** is readily replaced by **4** to give $[Ir(trans\text{-}C_6H_5CH{=}CHCHO)(CO)(PPh_3)_2]ClO_4$ (**4** is then coordinated through the oxygen atom but not through the olefinic π-system) [14], whereas the ClO_4^- group in **3** can not simply be replaced by **4** [15*]. Thus **4** in **11** can readily be replaced by the ClO_4^- group to give **3**. A dihydridometal complex, $LnM(H)_2(O{=}CR_2)$, analogous to **11** was also suggested as the intermediate in the hydrogenation of carbonyl compounds to alcohols [16]. The reaction rates with $[Ir(CO)(PPh_3)_3]^+$ (**7** and **8**) were lower than those with **2** (Table 1) are probably due to the relative ease of formation of **10** since the ClO_4^- in **2** is more labile than PPh_3 in $[Ir(CO)(PPh_3)_3]^+$ [14,17,18].



Scheme 1. $L_3 = (CO)(PPh_3)_2$.

Isomerization and hydrogenation of 3-phenylprop-2-en-1-ol (1) with $Ir[ClO_4](CO)(PPh_3)_2$ (2) and $Ir(H)_2(ClO_4)(CO)(PPh_3)_2$ (3) under nitrogen and hydrogen at 25 °C. Complex **2** catalyzes the hydrogenation of **1** to give 3-phenylpropan-1-ol (**12**) at room temperature under an atmospheric pressure of hydrogen. The data in Table 3 unambiguously suggest that the hydrogenation proceeds by rapid formation of the



Scheme 2. Ir: $Ir(ClO_4)(CO)(PPh_3)_2$ (**2**), $Ir(H)_2$: $Ir(H)_2(ClO_4)(CO)(PPh_3)_2$ (**3**), **1**: $C_6H_5CH{=}CHCH_2OH$, **4**: $C_6H_5CH{=}CHCHO$, **5**: $C_6H_5CH{=}CHCH_3$, **6**: $C_6H_5CH_2CH_2CHO$, **12**: $C_6H_5CH_2CH_2CH_2OH$.

isomerization product (**6**) which is then slowly hydrogenated to give **12** (eq. 9). Under a hydrogen pressure of more than 5 atm, the hydrogenation becomes so rapid that no isomerization product (**6**) is detected in the reaction mixture.

$$\underset{(1)}{C_6H_5CH{=}CHCH_2OH} \xrightarrow[\text{fast}]{2\ H_2} \underset{(6)}{C_6H_5CH_2CH_2CHO} \xrightarrow[\text{slow}]{2\ H_2} \underset{(12)}{C_6H_5CH_2CH_2CH_2OH} \qquad (9)$$

It is most likely that complex **3** is the actual catalyst for the isomerization of **1** to **6** in eq. 9 since **2** readily reacts with H_2 quantitatively to give **3** [8]. The isomerization of **1** with **2** under nitrogen (eq. 1 and Table 1) can also be catalyzed by **3** which is produced by the dehydrogenation of **1** with **2**. A similar suggestion has been made before; the six-coordinated dihydrides, $[Rh(H)_2L_2S_2]^+$ (but not $[RhL_2S_2]^+$) were indeed active catalysts for the isomerization of olefins in the presence of $[L_2RhCl]_2$ and Ag^+ under H_2 in solvent S (acetone, tetrahydrofuran, 2-methoxyethanol) [19].

Complex **3** does not seem to lose H_2 during the isomerization of **1** under nitrogen since from Table 2 it can be seen that the mole ratio of **(5 + 6)/3** is singificantly larger than 1.0 when the ratio of **1/3** is 2 or larger. Complex **3** loses H_2 probably by the reductive elimination, **3** → **2** + H_2 which is slow at 25 °C but may be significant for longer reaction times. When the ratio of **1/3** is larger than 4 and the reaction time is longer, dehydrogenation of **1** takes place (Table 2). This dehydrogenation is evidently catalyzed by **2**, which is produced in the hydrogenolysis of **1** with **3** and in the H_2 elimination of **3**. Scheme 2 summarizes the catalytic reactions of **1** with **2** and **3** under nitrogen and hydrogen.

It was found that the rates of isomerization of **1** and **1D** in the presence of **2** under hydrogen to the carbonyl compounds are practically identical within experimental error. This suggests that the first step of the isomerization is the slow migration of the double bond to give the enol, **13**, which undergoes fast tautomerization to give **6** (eq. 10). The migration of the double bond in **1** induced by **3** to give **13** (eq. 10), probably proceeds via the formation of monohydridoalkyliridium(III)

$$\underset{(1)}{C_6H_5CH{=}CHCH_2OH} \xrightarrow{\text{slow}} \underset{(13)}{C_6H_5CH_2CH{=}CHOH} \xrightarrow{\text{fast}} \underset{(6)}{C_6H_5CH_2CH_2CHO} \qquad (10)$$

Table 3

Isomerization and hydrogenation of 3-phenylprop-2-en-1-ol (**1**) (6.0 mmol) with $Ir(ClO_4)(CO)(PPh_3)_2$ (**2**) (0.2 mmol) in $CDCl_3$ (5.0 ml) at 25 °C under hydrogen (PH_2) + vapor pressure of the solution = 1 atm).

Time (h)	Product (%)	
	$C_6H_5CH_2CH_2CHO$ (**6**)	$C_6H_5CH_2CH_2CH_2OH$ (**12**)
3	100	0
10	75	25
28	15	85

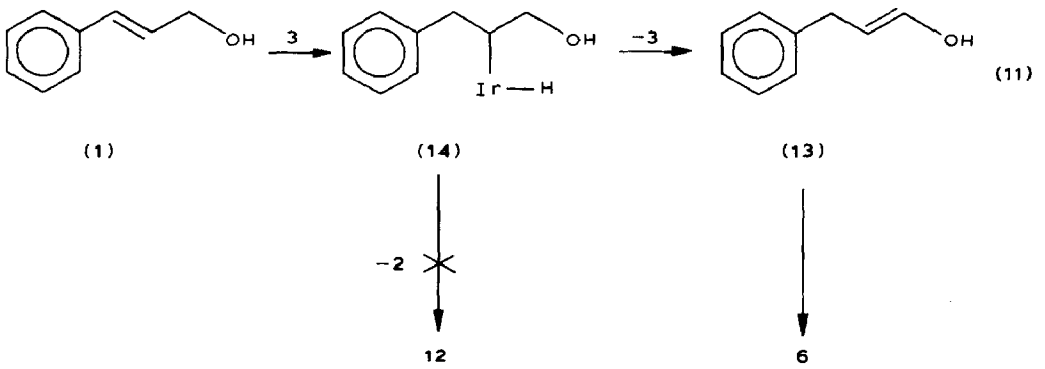
complex, **14** (eq. 11). Thus it was somewhat unexpected not to find the hydrogenation product product (**12**) during the isomerization of **1** to **6** (Table 3). This may be due to the fact that the β-hydrogen elimination (**14** → **3** + **13**) is much faster than the reductive elimination (**14** → **2** + **12**). Similar results have been obtained in the catalytic reactions of 3-phenylprop-1-ene (**15**) with **3** under hydrogen, that is, the double bond migration (**15** → 3-phenylprop-2-ene) is faster than the hydrogenation (**15** → 3-phenylpropane).

Experimental

Caution. Perchlorate salts of transition metal complexes containing organic ligands are potentially explosive [20].

The ^1H NMR spectra were measured on a Varian 60 MHz (EM-360A) or Bruker WP 80 MHz spectrometer. IR spectra were recorded on a Shimadzu IR-440 and mass spectra were recorded on a JEOL JMS-DX303 spectrometer (70 eV). All manipulations were carried out by use of Schlenk type glassware under nitrogen or hydrogen.

3-Phenylprop-2-en-1-ol (**1**), 3-pehnylprop-2-enal (**4**), 3-phenylprop-2-ene (**5**), 3-phenylpropanal (**6**), 3-phenylpropan-1-ol (**12**) and CD_3OD were purchased from Aldrich and used without further purification. $Ir(ClO_4)(CO)(PPh_3)_2$ (**2**), $Ir(H)_2(ClO_4)(CO)(PPh_3)_2$ (**3**), $[Ir(CO)(PPh_3)_3]ClO_4$ (**7**) and $[Ir(CO)(PPh_3)_3]BF_4$ (**8**) were prepared by published procedures [7,8,18].



Preparation of 3-phenylprop-2-en-1-ol-OD (1D). A solution of 3-phenylprop-2-en-1-ol (**1**, 5.0 g) in CD_3OD (99.8%, 5.0 ml) was stirred for 30 min under nitrogen at 25 °C, and volatile materials (CD_3OD and CD_3OH) were removed by vacuum distillation to yield pale-yellow crystals whose ^1H NMR spectrum showed that ca. 80% of the hydroxyl hydrogen of **1** had been replaced by deuterium to give **1D** ($C_6H_5CH{=}CHCH_2OD$). The above H–D exchange procedure was repeated another two times using 1.0 ml of CD_3OD. The ^1H NMR spectrum of the final product (m.p. 35 °C) in $CDCl_3$ showed that the product contains 90% of **1D**.

Isolation of [Ir(trans-$C_6H_5CH{=}CHCHO$)(CO)(PPh_3)$_2$]ClO_4 from the reaction of 3-phenylprop-2-en-1-ol (1) with Ir(ClO_4)(CO)(PPh_3)$_2$ (2). A solution of **1** (0.6 g, 4.5 mmol) and **2** (0.12 g, 0.15 mmol) in benzene (30 ml) was stirred under nitrogen at 25 °C. Light yellow microcrystals began to separate within 30 min. The crystals were collected by filtration, washed with benzene (20 ml) and dried in vacuum (0.08 g, 60%). The product was identified as [Ir(*trans*-$C_6H_5CH{=}CHCHO$)(CO)(PPh_3)$_2$]ClO_4 by comparison of its spectral (^1H NMR, IR, electronic absorption) data and molar conductance with those previously reported [14].

Analyses of products, 3-phenylprop-2-enal (4), 3-phenylprop-2-ene (5), 3-phenylpropanal (6), 3-phenylpropan-1-ol (12), H_2O, HDO and D_2O. The identity of **4**, **5**, **6** and **12** was established by comparison of the ^1H NMR spectra with those of authentic samples. Yields of the products were determined by comparing the signals in the ^1H NMR of the product mixtures. The presence of H_2O was indicated by use of Karl Fischer reagent. HDO and D_2O were detected by mass spectroscopy.

Reaction of 3-phenylprop-2-en-1-ol (1) with Ir(ClO_4)(CO)(PPh_3)$_2$ (2) under nitrogen. A solution of **1** (0.8 g, 6.0 mmol) and **2** (0.16 g, 0.2 mmol) in $CDCl_3$ (5.0 ml) was stirred under nitrogen at 25 °C. A 0.5 ml portion of the reaction mixture was removed from the reaction vessel and ^1H NMR measurements were carried out at intervals to find out when most of **1** had disappeared. H_2O analysis was carried out as soon as the reaction was complete.

Reactions of 3-phenylprop-2-en-1-ol (1) with Ir(H)$_2$(ClO_4)(CO)(PPh_3)$_2$ (3), [Ir(CO)(PPh_3)$_3$]ClO_4 (7), and [Ir(CO)(PPh_3)$_3$]BF_4 (8) under nitrogen. These reactions were carried out in the same manner as that described for the reaction of **1** with **2**.

Reaction of 3-phenylprop-2-en-1-ol-OD (1D) with Ir(ClO_4)(CO)(PPh_3)$_2$ (2) under nitrogen. This reaction was carried out in the same manner as that described for the reaction of 1 with 2.

Reaction of 3-phenylprop-2-en-1-ol (1) with Ir(ClO_4)(CO)(PPh_3)$_2$ (2) in the presence of excess ClO_4^-. To a solution of **1** (0.8 g, 6.0 mmol) in $CDCl_3$ (5.0 ml) was added $NaClO_4$ (ca. 1.0 g) and the mixture was stirred for 10 min. Undissolved $NaClO_4$ was removed by filtration before complex **2** (0.16 g, 0.2 mmol) was added to the solution, which was then stirred under nitrogen at 25 °C. Products were analyzed by ^1H NMR measurements.

Reaction of 3-phenylprop-2-en-1-ol (1) with Ir(ClO_4)(CO)(PPh_3)$_2$ (2) under hydrogen. This reaction was carried out under hydrogen (PH_2) + vapor pressure of the solution = 1 atm) in the same manner as that described for the reaction of **1** with **2**.

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13 $C_6H_5CH{=}CHCH_2OD$ (**1D**) prepared in the course of this study contains ca. 10% of unlabeled $C_6H_5CH{=}CHCH_2OH$ (**1**) (see Experimental).

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