Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 12695–12701

[IrCl(cod)]$_2$-catalyzed direct oxidative esterification of aldehydes with alcohols

Syun-ichi Kiyooka,[a,*] Yosuke Wada,[a] Mahuyu Ueno,[a] Takeshi Yokoyama[b] and Reiko Yokoyama[b]

[a]*Department of Materials Science, Faculty of Science, Kochi University, Akebono-cho, Kochi 780-8520, Japan*
[b]*Department of Anesthesiology and Critical Care Medicine, Kochi Medical School, Oko-cho, Nankoku 783-8505, Japan*

Received 6 September 2007; revised 1 October 2007; accepted 1 October 2007
Available online 5 October 2007

Abstract—[IrCl(cod)]$_2$ catalyzed the oxidative esterification of a variety of aldehydes with methanol as a solvent in combination with K_2CO_3 under mild conditions (rt, 12 h). The oxidative esterification reaction of aliphatic aldehydes also took place with olefinic alcohols as reagents in toluene under similar conditions.

1. Introduction

From a viewpoint of green chemistry, transition metal-catalyzed oxidative esterification is expected to be a versatile procedure directly giving esters from aldehydes and alcohols. Such oxidative esterification reactions, however, have not been reported frequently until now.[1] The actual reaction providing esters has been considered to proceed through the oxidative addition of low-valency transition metal species to the oxygen–hydrogen bond of alcohol to give an alkoxide and the attack of the resulting alkoxy group on the aldehyde carbonyl coordinated to the metal followed by the β-hydride elimination from the metal-bound hemiacetal intermediate. The β-hydride elimination is the most important step in the sequential processes of the oxidative esterification. Recently, Cp* iridium complexes are attracting much attention for their effectiveness for the β-hydride elimination as an oxidation process of alkoxo complexes.[2] In order to clarify the oxidative esterification using iridium complexes, we applied [IrCl(cod)]$_2$ to the oxidative esterification of aldehydes with alcohols because the iridium complex is commercially available and known to be useful for a variety of catalytic reactions in organic synthesis.[3] We disclose herein an oxidative esterification of a variety of aldehydes with simple alcohols as solvents in the presence of a catalytic amount of [IrCl(cod)]$_2$ in combination with K_2CO_3 at rt. Furthermore, when alcohols having an olefinic moiety were used as a reagent in toluene, the oxidative esterification reaction of aliphatic aldehydes took place under similar conditions.

Keywords: [IrCl(cod)]$_2$; Oxidative esterification without oxidants; Direct esterification of aldehydes.
* Corresponding author. Tel.: +81 88 844 8295; fax: +81 88 844 8359; e-mail: kiyooka@cc.kochi-u.ac.jp

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.10.003

2. Results and discussion

2.1. Iridium-catalyzed oxidative esterification of aldehydes with solvent alcohols

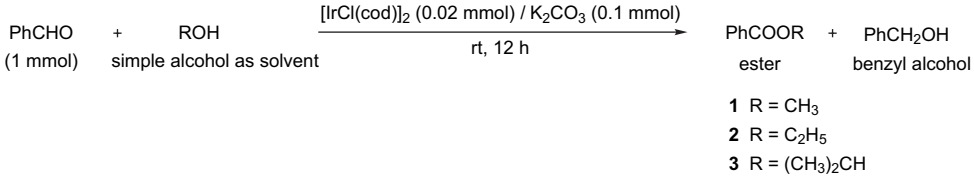
When benzaldehyde was stirred overnight in methanol in the presence of [IrCl(cod)]$_2$, the acetal, PhCH(OCH$_3$)$_2$, was only obtained in a considerable yield. The iridium complex apparently works as a Lewis acid in the case. However, the addition of K_2CO_3 under the same conditions dramatically altered the reaction course. It converted [IrCl(cod)]$_2$ to its alkoxo complex at rt.[2–4] Thus, the reaction of benzaldehyde with a large excess of methanol in the presence of [IrCl(cod)]$_2$ in combination with K_2CO_3 resulted in an oxidative esterification to give the corresponding ester. When benzaldehyde (1 mmol) was stirred overnight in methanol (1 mL) with [IrCl(cod)]$_2$ (0.02 mmol) and K_2CO_3 (0.1 mmol), a mixture of the ester and benzyl alcohol was obtained in 47% yield (Eq. 1, entry 1 in Table 1); the yield is calculated on the basis of the starting aldehyde. The ratio of the ester to benzyl alcohol was almost 1:1. The result allows us to consider the two different reactions, i.e., the esterification and the reduction, which coincidentally took place in a catalytic cycle. The reaction of benzaldehyde with simple alcohols as solvents was investigated, as shown in Table 1. The optimal quantity of methanol was adequate to be 2 mL (entry 2). When the quantity of methanol was used in large excess, the ratio of benzyl alcohol to ester was increased owing to the enhanced reduction of benzaldehyde (entry 3). A lower loading of the catalyst (1 mol %) resulted in a moderate yield (entry 4). Although a considerable amount of ethyl acrylate was added to the reaction mixture as hydrogen acceptor[1e] in order to reduce the reduction to benzyl alcohol, the result was not improved. At an elevated temperature the reduction

Table 1. Iridium-catalyzed oxidative esterification of benzaldehyde (1 mmol) with a large excess of simple alcohols under mild conditions at rt for 12 h in the presence of $[IrCl(cod)]_2$ and K_2CO_3 (Eq. 1)

Entry	$[IrCl(cod)]_2$ (mmol)	Solvent ROH (mL)	Yield[a] (%)	Ratios of ester and benzyl alcohol[b]
1	0.02	CH_3OH (1)	47 (**1**)	1:1.1
2	*0.02*	*CH_3OH (2)*	*87 (**1**)*	*1:1.1*
3	0.02	CH_3OH (5)	85 (**1**)	1:1.5
4	0.01	CH_3OH (2)	78 (**1**)	1:1.2
5[c]	0.02	CH_3OH (2)	82 (**1**)	1:1.8
6	0.02	C_2H_5OH (2)	57 (**2**)	1:3.2
7	0.02	$(CH_3)_2CHOH$ (2)	13 (**3**)	1:2.6

[a] The isolated yields are shown as a sum of the ester and benzyl alcohol.
[b] The ratios were obtained from their ^1H NMR spectra.
[c] The reaction was carried out under reflux conditions.

preferentially took place presumably owing to the hydride source supplied increasingly by the β-hydride elimination from the coordinated solvent methanol (entry 5). When ethanol was used, the reaction proceeded increasing the ratio of the reduction to benzyl alcohol (entry 6). It is noteworthy that ethanol is more rapidly oxidized by the iridium complex, compared with methanol in supplying more hydride species. On the other hand, the reaction with isopropanol resulted in a low yield, presumably depending on the lower nucleophilicity owing to the steric property as a secondary alcohol (entry 7).

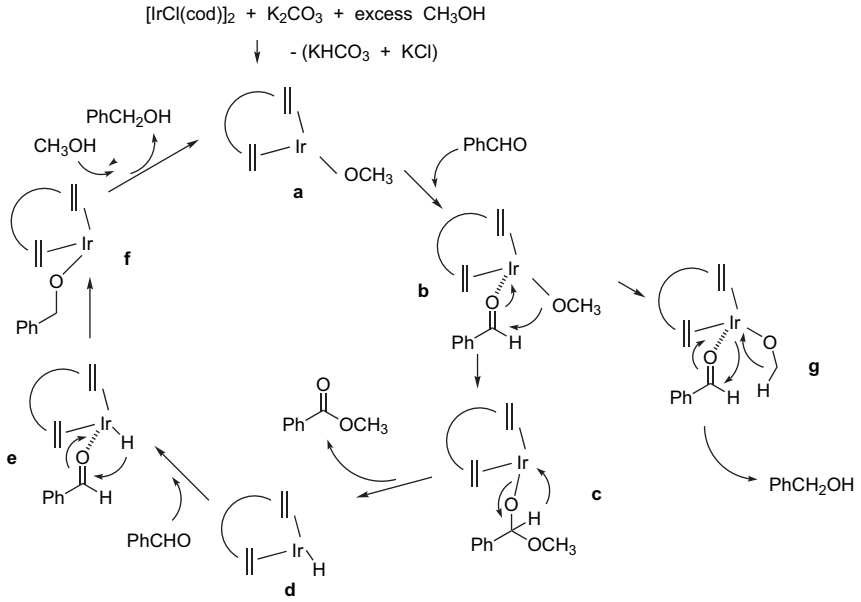


(1)

The iridium-catalyzed oxidative esterification reaction can be explained, as shown in Scheme 1. A large excess of methanol feasibly converts $[IrCl(cod)]_2$ to its iridium methoxo intermediate **a** by the assistance of K_2CO_3. Benzaldehyde coordinates to the intermediate to give the species **b** as the carbonyl function being activated by the metal. The following intramolecular nucleophilic migration of methoxy group leads to the hemiacetal species **c**. The β-hydride elimination at the species **c** produces the ester and the resulting hydride species **d**. The iridium hydride (**d**) can reduce benzaldehyde to give benzyl alcohol (via **e**). The intermediate **a** is recovered by solvolysis of the species **f** with excess methanol in delivering benzyl alcohol. Excess reduction of benzaldehyde might proceed by another iridium hydride species, probably supplied by an alternative hydride transfer from the coordinated alkoxo intermediate **g**.

Although the hydride transfer (redox) processes involving the intermediates **c**, **e**, and **g** are supposed to be in equilibrium, the large excess of solvent methanol provides a driving force for the catalytic cycle.

The result of the iridium-catalyzed oxidative esterification of a variety of aldehydes with methanol is summarized in



Scheme 1. A plausible reaction mechanism of the oxidative esterification of benzaldehyde with excess methanol accompanied by the reduction of benzaldehyde. (Coordinated solvents to the iridium metal are omitted from the scheme for its simplicity.)

Table 2. Iridium-catalyzed oxidative esterification of a variety of aldehydes with methanol (Eq. 2)

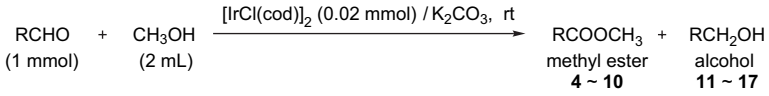
Entry	Aldehydes	K_2CO_3 (mmol)	Reaction time (h)	Yield[a] (%)	Ratios of ester and alcohol[b]
1	*p*-Tolualdehyde	0.1	12	60 (**4**+**11**)	1:1
2	*p*-Tolualdehyde	0.1	24	84 (**4**+**11**)	1:1
3	*p*-Nitrobenzaldehyde	0.1	12	78 (**5**+**12**)	1:1
4	2-Naphthaldehyde	0.1	24	62 (**6**+**13**)	1:1
5	2-Naphthaldehyde	0.3	24	82 (**6**+**13**)	1:1
6	1-Naphthaldehyde	0.1	24	20 (**7**+**14**)	1:2.1
7	1-Naphthaldehyde	0.3	24	65 (**7**+**14**)	1:3.6
8	4-Phenylbenzaldehyde	0.1	24	55 (**8**+**15**)	1:1.1
9	Hydrocinnamaldehyde	0.1	30	54 (**9**+**16**)	1:1.3
10	Hydrocinnamaldehyde	0.3	30	88 (**9**+**16**)	1:1.5
11	Cinnamaldehyde	0.1	24	46 (**10**+**17**)	1:1.2

[a] The isolated yields are shown as a sum of the ester and benzyl alcohol.
[b] The ratios were obtained from their ^{1}H NMR spectra.

Table 2 (Eq. 2). Long reaction time is occasionally requested for good yields comparable with that of benzaldehyde (entry 2). The yields were furthermore improved by increasing the quantity of K_2CO_3 (entries 5, 7, and 10). The reduction to the corresponding alcohol was preferentially observed with respect to 1-naphthaldehyde having some steric bulkiness owing to retardation of the alkoxide attack (entries 6 and 7). Similarly, less reactive hydrocinnamaldehyde as a representative of aliphatic aldehydes resulted in a moderate yield with a slight excess of the alcohol (entries 9 and 10).

2.2. Iridium-catalyzed oxidative esterification reaction of aldehydes with olefinic alcohols

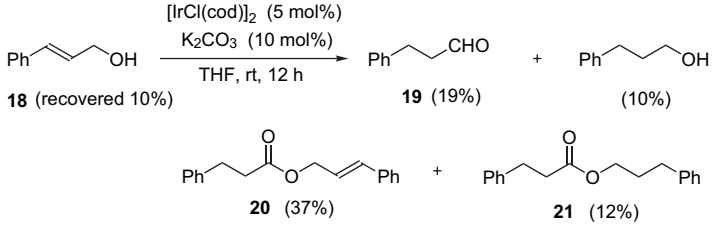
The transition metal-catalyzed isomerization of allylic alcohols to the corresponding carbonyl compounds is considered to proceed via a process involving hydrogen 1,3-shift with a hydrido-π-allylic intermediate (**a**) and the sequential ketonization through a hydrido-π-oxyallylic intermediate (**b**) as depicted in Scheme 2.[7] Iridium complexes are known to be effective for the isomerization of allylic alcohols to aldehydes and ketones.[8,9,10] The isomerization of allylic alcohol



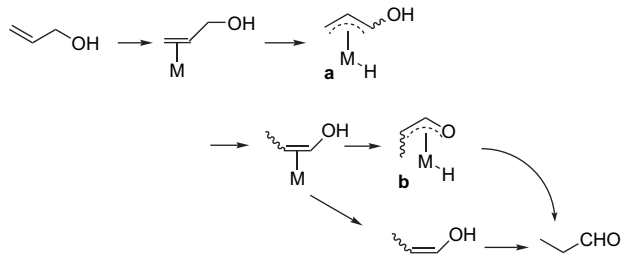
(2)

We tried the oxidative esterification using simple alcohols as substrates, but the formation of the ester could not be appreciated in the reaction of benzaldehyde with methanol as a substrate (2 mol equiv) in THF and toluene. Under similar conditions, the reactions with 3-phenyl-1-propanol and 1-methyl-1-propanol also did not proceed at all. Even 2-pyridylmethanol did not work, which seems to be effective for precoordination to transition metal centers.[5] However, it has been reported that alcohols, in which two alcohol functional groups are converged, undergo the oxidative esterification mediated by Cp* iridium complexes to give the corresponding lactones.[6a,b] Alcohols obtained directly from aldehydes are effective for Tishchenko dimerization to give esters in the presence of an Ir–ligand bifunctional catalyst, which was in situ prepared from the corresponding Ir complex and 2-propanol. The Ir-catalyzed Tishchenko reaction seems to proceed in a manner similar to Scheme 1.[6c,d]

by $[IrCl(cod)]_2$ was reported to propanal along with byproducts: propene and diallyl ether.[10] When reinvestigated the iridium-catalyzed isomerization reaction of cinnamyl alcohol under mild conditions ($[IrCl(cod)]_2$ (5 mol %), rt, 12 h, THF) in combination with K_2CO_3 (10 mol %), we incidentally found the ester formation as a self-condensation in the iridium-catalyzed isomerization reaction, as shown in Eq. 3.[11] The formation of the esters formally corresponds to the esterification of hydrocinnamic acid with cinnamyl and hydrocinnamyl alcohols (**20** and **21**). The whole process of the ester formation must be followed by C–O bond formation and subsequent oxidation during the isomerization of the allylic alcohol to the corresponding alcohol. Consequently, it resulted in a novel iridium-catalyzed oxidative esterification of an aliphatic aldehyde with an olefinic alcohol in THF. This condensation might be possible essentially by the precoordination of the olefinic moiety of the alcohol to the iridium center, as an anchor effect.[12]

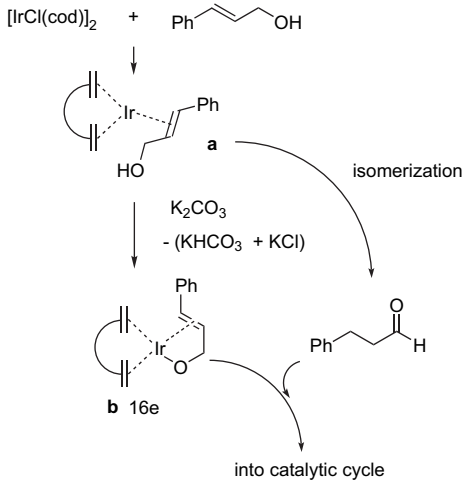


(3)



Scheme 2. Transposition of allylic alcohols into carbonyl compounds mediated by transition metal complexes.

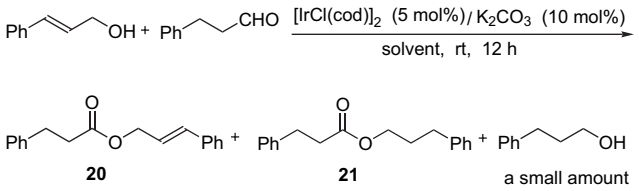
The early stage results in the formation of the iridium alkoxo complex (**b**), as shown in Scheme 3. Then, the resulting complex is introduced into a similar catalytic cycle, depicted in Scheme 1. In the catalytic cycle, the subsequent intramolecular migration of the resulting alkoxy group to the aldehyde, which was in advance produced via isomerization, takes place to afford an iridium acetal intermediate, followed by oxidative hydrogen transfer (β-hydrogen elimination) to give hydride iridium complexes delivering the product ester. The complexes can serve some reductions of the double bonds of the starting alcohol and the product ester and the aldehyde carbonyl. It is still uncertain whether the cod ligand remains unchanged over the process.[13]



Scheme 3. An effective precoordination of cinnamyl alcohol and the following formation of alkoxo complex at the early stage in the reaction of Eq. 3.

The condensation was continuously investigated in order to realize the general iridium-catalyzed oxidative esterification starting from a primary allylic alcohol and an aldehyde. The condensation reaction of hydrocinnamaldehyde with cinnamyl alcohol proceeded in a better yield of the same ester pair (**20** and **21**) along with 3-phenyl-1-propanol as a reduction product, compared with the reaction starting with only cinnamyl alcohol (Table 3). The best result was obtained in toluene with a 1:2 molar ratio of the starting aldehyde to alcohol (entry 3). Acetonitrile was inadequate for the reaction, probably owing to its strong coordination ability as covering the catalytic center (entry 4). Although a large excess of 2-norbornene was added in order to prevent the reduction of the olefinic ester to the saturated one under

Table 3. Iridium-catalyzed oxidative esterification of hydrocinnamaldehyde with cinnamyl alcohol



Entry	Aldehyde/alcohol	Solvents	Yields[a] of **20** and **21**
1	1:1	THF	46 (3:1)
2	1:2	THF	60 (2:1)
3	*1:2*	*Toluene*	*97 (3:2)*
4	1:2	CH_3CN	No reaction

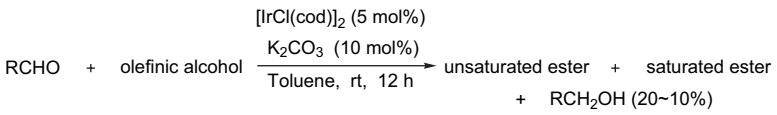
[a] The isolated yields were determined, based on the starting aldehyde, although the amount of the aldehyde might be partially increased by isomerization of cinnamyl alcohol during the reaction.

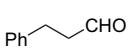
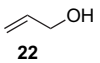
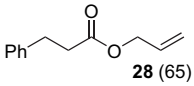
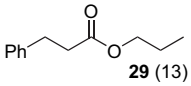
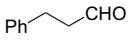
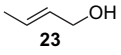
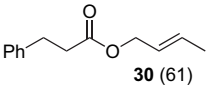
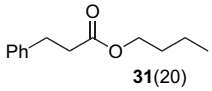
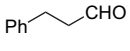
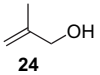
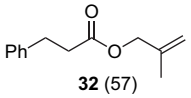
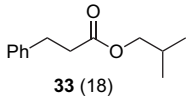
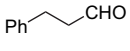
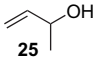
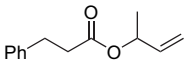
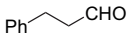
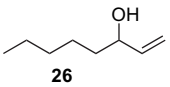
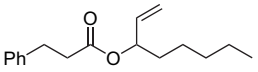
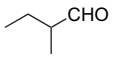
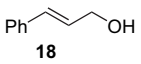
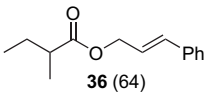
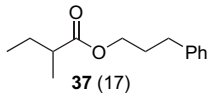
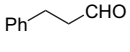
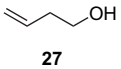
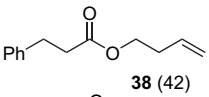
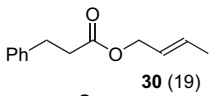
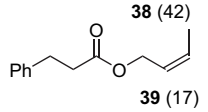
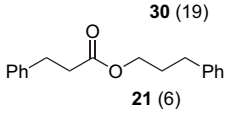
the optimal conditions,[14] the yield unfortunately decreased to 25% in spite of the expected improvement of the ratio of **20** to **21** to be 9:1.

Cross-condensations between allylic alcohols and aldehydes having different structures may be possible because iridium-catalyzed allylic isomerization is dispensable for this oxidative esterification. The cross-condensations were carried out using hydrocinnamaldehyde and 2-methylbutyraldehyde as typical primary and secondary aliphatic aldehydes, as shown in Table 4. In practice, a variety of primary and secondary allylic alcohols underwent the iridium-catalyzed oxidative esterification reaction to afford the corresponding esters in good yields despite the structural difference of the allylic alcohols (entries 1–6). When secondary allylic alcohols were used, the obtained products were only unsaturated esters because of the steric hindrance against the reduction (entries 4 and 5). Furthermore, an interesting feature of this reaction was found that an olefinic alcohol (**27**) having a double bond far from the hydroxy function exactly works (entry 7). Presumably the remote double bond works effectively for the precoordination to the iridium center to form the resulting alkoxo complex and allows the attack of the pendant alkoxo moiety to the coordinated aldehyde to make the subsequent C–O bond formation possible. The condensation reaction with **27** allowed to give a small amount of the ester (**21**) from 3-phenyl-1-propanol as a reduction product of the starting aldehyde because the main condensation reaction is relatively slow in comparison with the corresponding reaction with allylic alcohols. Double bond isomerization in the product esters was also observed but in this case the double bonds could not be reduced.

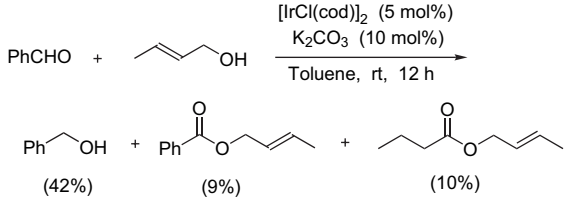
In addition, aromatic aldehyde showed slightly different behavior in the reaction. The reaction of benzaldehyde with crotyl alcohol gave a large amount of benzyl alcohol (42%) along with a small amount of the expected ester (9%) and the ester (10%) from the aldehyde via the isomerization of the starting alcohol (Eq. 4). The electron-attractive character of the aromatic moiety, compared to that of aliphatic one, might be suitable for the reduction under the reaction conditions.

Table 4. Iridium-catalyzed oxidative esterification reaction with a variety of olefinic alcohols[a]



Entry	Aldehydes	Alcohols	Esters (% yield)[b]
1		 **22**	 **28** (65)  **29** (13)
2		 **23**	 **30** (61)  **31**(20)
3		 **24**	 **32** (57)  **33** (18)
4		 **25**	 **34** (82)
5		 **26**	 **35** (80)
6		 **18**	 **36** (64)  **37** (17)
7		 **27**	 **38** (42)  **30** (19)  **39** (17)  **21** (6)

[a] The reaction conditions of entry 3 in Table 3 were used.
[b] Isolated yields.



(4)

3. Conclusion

In summary, a variety of aldehydes are directly transferred in simple alcohol solvents in the manner of the oxidative esterification being accompanied by the sequential reduction of the aldehydes under mild conditions with catalytic amounts of $[IrCl(cod)]_2$ in the presence of K_2CO_3. On the other hand, the starting alcohols having an olefinic moiety work well as substrates in the oxidative esterification reaction of aliphatic aldehydes to give the corresponding esters in good yields. As long as the starting alcohols are used as solvents, the alcohols do not need to furnish an olefinic moiety for the reaction.

4. Experimental

4.1. General

All solvents were dried by standard methods. All reactions were carried out under an inert atmosphere. Merck silicagel 60 (230–400 mesh) was used for flash column chromatography. All products obtained in the iridium-catalyzed oxidative esterification are known esters, which were ascertained by NMR analyses: ^1H and ^{13}C NMR spectra were recorded with a Jeol JNM-LA 400 spectrometer with tetramethylsilane used as an internal standard.

4.2. Typical procedure for the oxidative esterification in simple alcohols

To a mixture of $[IrCl(cod)]_2$ (14 mg, 0.02 mmol) and K_2CO_3 (14 mg, 0.1 mmol) was added methanol (2 mL) under Ar. After stirring for 10 min at rt, the solution turned pale yellow. Aldehyde (1 mmol) was added dropwise to the solution. The color of the solution gradually changed dark. The reaction mixture was stirred at rt overnight and quenched with saturated NH_4Cl (5 mL). The resulting

aqueous solution was evaporated in vacuo to a half volume. Next, ether (10 mL) was added to the residue and the organic layer was separated. The aqueous layer was extracted with ether (10 mL×2). The combined organic layers were dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude residue was purified by flash column chromatography on silica-gel to give the ester and the alcohol.

4.2.1. Methylbenzoate 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (3H, s), 7.41 (2H, t, J=7.8 Hz), 7.53 (1H, t, J=7.8 Hz), 8.02 (2H, d, J=7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.0, 128.3 (2C), 130.0 (2C), 130.1, 132.9, 167.1.

4.2.2. Methyl 4-methylbenzoate 4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (3H, s), 3.90 (3H, s), 7.23 (2H, d, J=7.8 Hz), 7.93 (1H, d, J=7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 51.9, 127.4, 129.1 (2C), 129.6 (2C), 143.5, 167.2.

4.2.3. Methyl 4-nitrobenzoate 5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (3H, s), 8.22 (2H, d, J=9.0 Hz), 8.30 (2H, d, J=9.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.8, 123.5 (2C), 130.7 (2C), 135.4, 150.4, 165.1.

4.2.4. Methyl 2-naphthoate 6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (3H, s), 7.55 (1H, t, J=6.8 Hz), 7.60 (1H, t, J=6.8 Hz), 7.88 (2H, d, J=8.6 Hz), 7.95 (1H, d, J=7.8 Hz), 8.06 (1H, d, J=8.6 Hz), 8.62 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 125.2, 126.6, 127.4, 127.8, 128.1, 128.2, 129.4, 131.1, 132.5, 135.5, 167.3.

4.2.5. Methyl 1-naphthoate 7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (3H, s), 7.52 (2H, quintet, J=7.8 Hz), 7.63 (1H, t, J=7.1 Hz), 7.88 (1H, d, J=8.3 Hz), 8.02 (1H, d, J=8.3 Hz), 8.18 (1H, d, J=7.3 Hz), 8.91 (1H, d, J=8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 124.5, 125.8, 126.2, 127.0, 127.8, 128.5, 130.2, 131.0, 133.4 (2C), 168.0.

4.2.6. Methyl 4-phenylbenzoate 8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (3H, s), 7.39 (1H, t, J=7.1 Hz), 7.47 (2H, t, J=7.1 Hz), 7.64 (4H, m), 8.10 (2H, d, J=8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.1, 127.0 (2C), 127.2 (2C), 128.1, 128.8, 128.9 (2C), 130.1 (2C), 139.9, 145.5, 167.0.

4.2.7. Methyl hydrocinnamate 9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (2H, t, J=7.8 Hz), 2.95 (2H, t, J=8.0 Hz), 3.67 (3H, s), 7.19–7.31 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 35.7, 51.6, 126.2, 128.2 (2C), 128.5 (2C), 140.5, 173.3.

4.2.8. Methyl cinnamate 10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (3H, s), 6.44 (1H, d, J=16.0 Hz), 7.27 (3H, m), 7.39 (2H, m), 7.70 (1H, d, J=16.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.7, 117.7, 128.0 (2C), 128.7 (2C), 130.3, 134.3, 144.8, 167.4.

4.3. Typical procedure for the oxidative esterification with olefinic alcohols

Toluene (2 mL) was added to a mixture of $[IrCl(cod)]_2$ (34 mg, 0.05 mmol) and K_2CO_3 (14 mg, 0.1 mmol) under Ar. Aldehyde (1 mmol) and alcohol (2 mmol) were slowly added to the solution. The reaction mixture was stirred at rt for 12 h. The reaction was quenched with saturated NH_4Cl (5 mL). The organic layer was separated and the aqueous layer was extracted with ether (10 mL ×3). The combined organic layers were dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude residue was purified by flash column chromatography on silica-gel to give the resulting esters.

4.3.1. (2*E*)-3-Phenyl-2-propenyl 3-phenylpropionate 20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (2H, t, J=7.8), 2.97 (2H, t, J=7.8 Hz), 4.27 (2H, dd, J=1.2, 5.4 Hz), 6.20–6.27 (1H, m), 6.11 (1H, d, J=15.9 Hz), 7.15–7.38 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.8, 35.7, 64.8, 123.0, 126.1, 126.5 (2C), 127.9, 128.1 (2C), 128.3 (2C), 128.4 (2C), 134.0, 136.0, 140.3, 172.4.

4.3.2. 3-Phenylpropyl 3-phenylpropionate 21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88–1.95 (2H, m), 2.62 (2H, t, J=7.8 Hz), 2.67 (2H, t, J=7.6 Hz), 2.97 (2H, t, J=7.8 Hz), 4.07 (2H, t, J=6.6 Hz), 7.15–7.38 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.0, 30.8, 32.0, 35.6, 63.6, 125.8, 126.1, 128.1 (2C), 128.2 (2C), 128.3 (4C), 140.3, 141.0, 172.6.

4.3.3. Propenyl 3-phenylpropionate 28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (2H, t, J=7.8 Hz), 2.97 (2H, t, J=7.8 Hz), 4.58 (2H, dt, J=1.3, 5.7 Hz), 5.22 (1H, dq, J=1.2, 10.3 Hz), 5.28 (1H, dq, J=1.5, 17.3 Hz), 5.84–5.94 (1H, m), 7.18–7.31 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 35.9, 65.1, 118.2, 126.2, 128.3 (2C), 128.5 (2C), 132.1, 140.4, 172.5.

4.3.4. Propyl 3-phenylpropionate 29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (3H, t, J=7.4 Hz), 1.59–1.64 (2H, m), 2.66 (2H, t, J=7.8 Hz), 2.98 (2H, t, J=7.8 Hz), 4.03 (2H, t, J=6.7 Hz), 7.18–7.31 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.3, 21.9, 31.0, 35.9, 66.1, 126.2, 128.3 (2C), 128.5 (2C), 140.5, 173.0.

4.3.5. (2*E*)-2-Butenyl 3-phenylpropionate 30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (3H, dd, J=1.2, 6.4 Hz), 2.63 (2H, t, J=7.8 Hz), 2.95 (2H, d, J=7.9 Hz), 4.50 (2H, dt, J=0.96, 6.6 Hz), 5.51–5.60 (1H, m), 5.69–5.81 (1H, m), 7.18–7.30 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 30.9, 35.9, 65.1, 125.0, 126.2, 128.2 (2C), 128.5 (2C), 131.4, 140.5, 172.7.

4.3.6. Butyl 3-phenylpropionate 31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (3H, t, J=7.4 Hz), 1.29–1.39 (2H, m), 1.54–1.61 (2H, m), 2.63 (2H, t, J=7.8 Hz), 2.95 (2H, t, J=7.9 Hz), 4.07 (2H, t, J=6.7 Hz), 7.18–7.30 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 18.9, 30.5, 30.8, 35.7, 64.1, 126.0, 128.2 (3C), 128.3, 140.4, 172.7.

4.3.7. 2-Methyl-2-propenyl 3-phenylpropionate 32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (3H, s), 2.70 (2H, t, J=7.7 Hz), 3.00 (2H, t, J=7.8 Hz), 4.53 (2H, s), 4.94 (1H, s), 4.96 (1H, s), 7.19–7.36 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 30.9, 35.8, 67.6, 126.1, 112.8, 128.2 (2C), 128.4 (2C), 139.8, 140.5, 172.4.

4.3.8. 2-Methylpropyl 3-phenylpropionate 33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (6H, d, J=6.8 Hz), 1.86–1.98 (1H, m), 2.66 (2H, t, J=7.6 Hz), 2.99 (2H, t, J=8.0 Hz),

3.88 (2H, d, J=6.8 Hz), 7.19–7.36 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0 (2C), 27.6, 30.9, 35.8, 70.5, 126.2, 128.2 (2C), 128.4 (2C), 140.4, 172.9.

4.3.9. 1-Methyl-2-propenyl 3-phenylpropionate 34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (3H, d, J=6.6 Hz), 2.63 (2H, t, J=7.8 Hz), 2.95 (2H, t, J=7.8 Hz), 5.11 (1H, dt, J=1.2, 10.5 Hz), 5.19 (1H, dt, J=1.22, 17.4 Hz), 5.32–5.38 (1H, m), 5.73–5.85 (1H, m), 7.16–7.30 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 30.9, 36.1, 70.9, 115.7, 126.2, 128.3 (2C), 128.4 (2C), 137.6, 140.5, 172.1.

4.3.10. 1-Octen-3-yl 3-phenylpropionate 35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (3H, t, J=6.8 Hz), 1.25–1.28 (6H, m), 1.48–1.63 (2H, m), 2.63 (2H, t, J=7.8 Hz), 2.95 (2H, t, J=7.8 Hz), 5.12 (1H, dt, J=0.96, 10.5 Hz), 5.17 (1H, dt, J=1.4, 17.3 Hz), 5.23 (1H, q, J=6.6 Hz), 5.70–5.78 (1H, m), 7.16–7.29 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.4, 24.6, 31.0, 31.5, 34.1, 36.1, 74.8, 116.4, 126.2, 128.2 (2C), 128.4 (2C), 136.6, 140.5, 172.1.

4.3.11. (2*E*)-3-Phenyl-2-propenyl 2-methylbutyrate 36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (3H, t, J=7.4 Hz), 1.17 (3H, d, J=6.8 Hz), 1.43–1.55 (1H, m), 1.65–1.75 (1H, m), 2.34–2.46 (1H, m), 4.74 (2H, dd, J=1.2, 6.3 Hz), 6.25–6.33 (1H, m), 6.55 (1H, d, J=15.9 Hz), 7.17–7.14 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 16.6, 26.8, 41.1, 64.7, 123.4, 126.6 (2C), 128.0, 128.6 (2C), 133.9, 136.2, 176.5.

4.3.12. 3-Phenylpropyl 2-methylbutyrate 37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (3H, t, J=7.5 Hz), 1.15 (3H, t, J=7.8 Hz), 1.43–1.55 (1H, m), 1.65–1.75 (1H, m), 1.92–1.99 (2H, m), 2.33–2.46 (1H, m), 2.69 (2H, t, J=7.7 Hz), 4.09 (2H, dt, J=1.2, 6.5 Hz), 7.17–7.41 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 16.6, 26.8, 30.3, 32.1, 41.1, 63.4, 126.0, 128.3 (2C), 128.4 (2C), 141.2, 176.8.

4.3.13. 3-Butenyl 3-phenylpropionate 38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (2H, q, J=6.4 Hz), 2.62 (2H, t, J=8.0 Hz), 2.95 (2H, t, J=8.0 Hz), 4.12 (2H, t, J=6.4 Hz), 5.05 (1H, dd, J=1.6, 10.4 Hz), 5.09 (1H, dd, J=1.6, 16.8 Hz), 5.75 (1H, ddt, J=6.8, 10.4, 16.8 Hz), 7.15–7.30 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.0, 33.0, 35.9, 63.5, 117.2, 126.2, 128.3 (2C), 128.5 (2C), 134.0, 140.5, 173.0.

4.3.14. (2*Z*)-2-Butenyl 3-phenylpropionate 39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (1H, d, J=6.8 Hz), 2.59 (2H, t, J=7.8 Hz), 2.95 (2H, t, J=7.8 Hz), 4.64 (2H, d, J=7.2 Hz), 5.50–5.60 (1H, m), 5.70–5.80 (1H, m), 7.15–7.30 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 30.9, 35.9, 60.1, 124.2, 126.2, 128.3 (2C), 128.5 (2C), 129.6, 140.5, 173.0.

Acknowledgements

We thank a Grant-in-Aid for Scientific Research of Japan Society for the Promotion of Science.

References and notes

1. Pd: (a) Lloyd, W. G. *J. Org. Chem.* **1967**, *32*, 2816–2819; (b) Tamaru, Y.; Yamada, Y.; Inoue, K.; Yamamoto, Y.; Yoshida, Z. *J. Org. Chem.* **1983**, *48*, 1286–1292; Ru: (c) Murahashi, S. I.; Ito, K.; Naota, T.; Maeda, Y. *Tetrahedron Lett.* **1981**, *22*, 5327–5330; (d) Murahashi, S. I.; Naota, T.; Ito, K.; Maeda, Y.; Taki, H. *J. Org. Chem.* **1987**, *52*, 4319–4327; Rh: (e) Grigg, R.; Mitchell, T. R. B.; Sutthivaiyakit, S. *Tetrahedron* **1981**, *37*, 4313–4319; (f) Krug, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 1674–1679; Ni: (g) Han, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1997**, *119*, 8135–8136.
2. (a) Bernard, K. A.; Rees, W. M.; Atwood, J. D. *Organometallics* **1986**, *5*, 390–391; (b) Fujita, K.; Furukawa, S.; Yamaguchi, R. *J. Organomet. Chem.* **2002**, *649*, 289–292; (c) Hanasaka, F.; Fujita, K.; Yamaguchi, R. *Organometallics* **2004**, *23*, 1490–1492.
3. (a) Ishii, Y.; Sakaguchi, S. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 909–920; (b) Taguchi, K.; Nakagawa, H.; Hirabayashi, T.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc.* **2004**, *126*, 72–73; (c) A variety of Ir complexes are summarized in 'Recent advances in iridium-catalyzed organic synthesis': Takeuchi, R.; Kezuka, S. *J. Synth. Org. Chem. Jpn.* **2007**, *65*, 652–664.
4. (a) The Ir complexes activated by alkyl phosphines are known to undergo the oxidative addition of aliphatic alcohols without bases even at low temperature: Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **2002**, *124*, 11456–11467; (b) $[IrCl(cod)]_2$ is known to be converted to $[Ir(cod)(OR)]_2$ in the presence of Na_2CO_3 in alcohol solvents: see Ref. 1f.
5. The chelation-assisted hydroesterification of alkenes with 2-pyridylmethanol was catalyzed by $Rh_4(CO)_{12}$: Yokota, K.; Tatamidai, H.; Fukumoto, Y.; Chatani, N. *Org. Lett.* **2003**, *5*, 4329–4331.
6. (a) Suzuki, T.; Morita, K.; Tsuchida, M.; Hiroi, K. *Org. Lett.* **2002**, *4*, 2361–2363; (b) Suzuki, T.; Morita, K.; Moritsuo, Y.; Hiroi, K. *Tetrahedron Lett.* **2003**, *44*, 2003–2006; (c) Suzuki, T.; Yamada, T.; Matsuo, T.; Watanabe, K.; Katoh, T. *Synlett* **2005**, 1450–1452; (d) Suzuki, T.; Matsuo, T.; Watanabe, K.; Katoh, T. *Synlett* **2005**, 1453–1455.
7. (a) Uma, R.; Davies, M.; Crévisy, C.; Grée, R. *Chem. Rev.* **2003**, *103*, 27–51; (b) Bergens, S. H.; Bosnich, B. *J. Am. Chem. Soc.* **1991**, *113*, 958–967.
8. Davies, S. G. *Organotransition Metal Chemistry, Applications to Organic Synthesis*; Pergamon: Oxford, 1982; pp 282–290.
9. (a) Baudry, D.; Ephritikhine, M.; Felkin, H. *Nouv. J. Chim.* **1977**, *2*, 355–356; (b) Ohmura, T.; Shirai, Y.; Yamamoto, Y.; Miyaura, N. *Chem. Commun.* **1998**, 1337–1338.
10. Pannetier, G.; Bonnaire, R.; Fougeroux, P. *J. Organomet. Chem.* **1971**, *30*, 411–419.
11. A preliminary report: Kiyooka, S.-i.; Ueno, M.; Ishii, E. *Tetrahedron Lett.* **2005**, *46*, 4639–4642.
12. The precoordination of olefinic moiety of allylic alcohol to the ruthenium center was postulated in the ruthenium-catalyzed reconstitutive condensation of allylic alcohols and terminal alkynes: Trost, B. N.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5579–5584.
13. Martín, M.; Sola, E.; Torres, O.; Plou, P.; Oro, L. A. *Organometallics* **2003**, *22*, 5406–5417.
14. Breton, D.; Stefan, J. P.; Dalobor, S. *J. Am. Chem. Soc.* **2004**, *126*, 6556–6557.