Selective Dimerization of Aldehydes to Esters Catalyzed by Zirconocene and Hafnocene Complexes

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Zirconocene and hafnocene complexes such as Cp_2MH_2 and $Cp_2M(Cl)H$ (M = Zr or Hf) were found to catalyze efficiently the selective dimerization of aldehydes to esters under mild conditions. Hafnocene complexes exhibited higher activity than the corresponding zirconocene complexes, while titanocene complexes were inert in the present reaction. The reaction was found to be markedly influenced by the structure of the aldehydes used. Cross-dimerization could be achieved by allowing Cp_2ZrH_2 or $Cp_2Zr(Cl)H$ to react with two different aldehydes whose reactivities are slightly different from each other.

Introduction

The Tishchenko reaction is well-known as the method for the preparation of esters from aldehydes[1] and has been studied in detail.[2-5] Although this method is usually carried out using aluminum alkoxides as catalysts, some catalytic systems such as $B(OH)_3$,[6] $LiWO_2$,[7] $Fe(CO)_4{}^{2-}$,[8] EtLnI (Ln = Pr, Nd, Sm),[9] and SmI_2[10,11] have also been reported to promote the dimerization of aldehydes to esters. Recently, hydroruthenium complexes such as $RuH_2(PPh_3)_4$ were reported to catalyze not only the dimerization of aldehydes to esters[12] but also the oxidative transformation of alcohols and diols to esters and lactones,[13] respectively.

Previously, we showed that zirconocene and hafnocene complexes such as Cp_2MH_2 (M = Zr or Hf) efficiently catalyze the hydrogen-transfer reaction of alcohols to carbonyl compounds (i.e., Meerwein–Ponndorf–Verley type reduction and Oppenauer oxidation).[14] We now find that group 4 metallocene complexes promote the selective dimerization of aldehydes to esters in fair to good yields under mild conditions. This system was extended to the cross-esterification of two different aldehydes whose reactivities are different from each other.

## 1. Homo-Dimerization of Aldehydes to Esters

3-Cyclohexene-1-carboxaldehyde (1) was chosen as a model substrate and allowed to react in the presence of group 4 metallocene complexes (eq 1). Table I shows the dimerization of 1 to (3-cyclohexenyl)methyl 3-cyclohexene-

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Table I. Dimerization of 3-Cyclohexene-1-carboxaldehyde (1) to (3-Cyclohexenyl)methyl 3-Cyclohexene-1-carboxylate (2) by Various Group 4 Metallocene Complexes[a]

run	catalyst	conv/%	yield/%
1	Cp_2ZrH_2	92	90
2	Cp_2HfH_2	95	87
3	$Cp_2Zr(H)Cl$	9	9
4[b]	$Cp_2Zr(H)Cl$	97	94
5	$Cp_2Hf(H)Cl$	90	67
6	Cp_2ZrCl_2	0	0
7	Cp_2HfCl_2	0	0
8	$Cp_2ZrCl_2/2n$-BuLi	97	93
9	$Cp_2HfCl_2/2n$-BuLi	100	95
10	$Cp_2TiCl_2/2n$-BuLi	13	6
11	Cp_2ZrCl_2/n-BuLi	82	80
12	Cp_2HfCl_2/n-BuLi	95	89

[a] 1 (5 mmol) was allowed to react under the influence of catalyst (5 mol %) at 0 °C for 0.5 h under Ar. [b] 17 °C, 8 h.

$$\text{(1)}$$
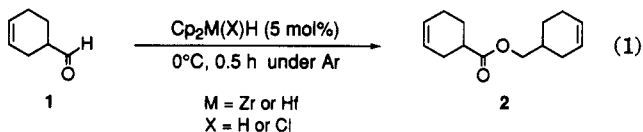
1-carboxylate (2) by a variety of zirconocene and hafnocene complexes.[15]

Under the influence of a catalytic amount of bis(η^5-cyclopentadienyl)zirconium dihydride (Cp_2ZrH_2), aldehyde 1 was converted into ester 2 at 0 °C with a short reaction time (0.5 h) in good yield. In a manner similar to that with Cp_2ZrH_2, the corresponding hafnocene complex, Cp_2HfH_2, readily catalyzed the dimerization of 1 to 2. Under these conditions, the catalytic activity of $Cp_2Zr(Cl)H$ was quite low compared with that of Cp_2ZrH_2, and 2 was formed in only 9% yield (run 3). However, when the reaction was carried out at higher temperature (17 °C) for 8 h, 2 was obtained in satisfactory yield (94%). Unlike $Cp_2Zr(Cl)H$, the corresponding hafnocene complex, $Cp_2Hf(Cl)H$, indicated higher catalytic activity than $Cp_2Zr(Cl)H$ to form 2 in 67% yield. Both Cp_2ZrCl_2 and Cp_2HfCl_2 were inert for the present reaction. Plausible low valent zirconocene and hafnocene complexes, Cp_2M (M = Zr or Hf), obtained by treating Cp_2MCl_2 with n-BuLi (2

(15) Although 2 gave a ¹³C-NMR consisting of 14 carbon signals, 2 was found to consist of an isomeric mixture of two diastereomers. It is because the analytical data of 2 were completely consistent with those of 2 prepared independently by the esterification of the corresponding acid and alcohol under acidic conditions, which leads to a mixture of two diastereoisomers.

Table II. Dimerization of Aldehydes to Esters Catalyzed by Cp$_2$MH$_2$ (M = Zr, Hf)^a

run	aldehyde	Cp$_2$MH$_2$ (M = Zr, Hf)	conv/%	ester (yield/%)
1	3a	Zr	70	4a (60)
2	3a	Hf	90	4a (78)
3^b	3b	Zr	88	4b (42)
4	3b	Hf	97	4b (57)
5	3c	Zr	94	4c (92)
6	3c	Hf	97	4c (92)
7	3d	Zr	84	4d (64)
8	3d	Hf	97	4d (92)
9^b	3e	Zr	72	4e (62)
10	3e	Hf	95	4e (84)
11	3f	Zr	92	4f (79)
12	3f	Hf	99	4f (80)
13^b	3g	Zr	10	4g (7)
14^b	3g	Hf	13	4g (9)

^{a} Aldehyde (5 mmol) was allowed to react with Cp$_2$MH$_2$ (M = Zr, Hf; 5 mol %) at 0 °C for 0.5 h under Ar. ^{b} 17 °C, 0.5 h.

equiv), catalyzed the dimerization of 1 to 2 in excellent yields, while the Cp$_2$TiCl$_2$/2n-BuLi system exhibited very little activity. It is interesting to note that the zirconocene and hafnocene complexes, derived from Cp$_2$ZrCl$_2$ and 1 equiv of n-BuLi, were also efficient, though the catalytic activities were slightly lower than the complexes obtained from Cp$_2$MCl$_2$ and 2 equiv of n-BuLi.

On the basis of these results, a variety of aldehydes were allowed to react under the influence of Cp$_2$ZrH$_2$ or Cp$_2$HfH$_2$ in the absence of solvent at 0 °C (eq 2). Representative results are shown in Table II.

$$\text{R-CHO} \quad \xrightarrow[\text{0°C, 0.5 h under Ar}]{\text{Cp}_2\text{ZrH}_2 \ (5 \ \text{mol\%})} \quad \text{R-COOCH}_2\text{-R} \qquad (2)$$
3 → 4

3, 4	R-	3, 4	R-
a	n-C$_3$H$_7$-	e	(CH$_3$)$_3$C-
b	n-C$_5$H$_{11}$-	f	⬡-
c	(CH$_3$)$_2$CH-	g	⬡(arom)-
d	CH$_3$(CH$_2$)$_2$CH(CH$_3$)-		

Linear aldehydes such as butanal (3a) and hexanal (3b) were slightly reluctant toward dimerization by Cp$_2$ZrH$_2$ to produce the corresponding esters, 4a and 4b, in fair yields, but the reactions proceeded readily using Cp$_2$HfH$_2$. Branched aldehydes, 2-methylpropanal (3c) and 2-methylpentanal (3d), having an alkyl substituent at the α-carbon, were similarly dimerized to produce 2-methyl-1-propyl 2-methylpropanoate (4c) and 2-methyl-1-pentyl 2-methylpentanoate (4d), respectively. Ester 4d consisted of about a 1:1 diastereoisomeric mixture. The esterification of an α,α-disubstituted aldehyde such as 2,2-dimethylpropanal (3e) was difficult, but when the reaction was carried out at room temperature (17 °C), 2,2-dimethyl-1-propyl 2,2-dimethylpropanoate (4e) was obtained in fair yield. Cyclohexanecarboxaldehyde (3f) afforded 1-cyclohexylmethyl cyclohexanecarboxylate (4f) in high yield. Unfortunately, benzaldehyde (3g) was quite difficult to convert into benzyl benzoate (4g) in satisfactory yield even at room temperature.
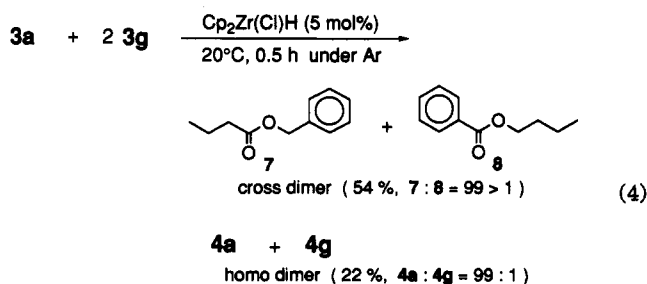
2. Cross-Dimerization of Aldehydes by Cp$_2$ZrH$_2$ and Cp$_2$Zr(Cl)H

The cross-esterification of two different aldehydes by the Tishchenko type reaction has been examined using several catalytic systems. However, it is difficult to achieve the reaction with high selectivity. Thus, we attempted the cross-dimerizations of 1:1 binary mixtures of butanal (3a) and various aldehydes in the presence of a catalytic amount of Cp$_2$Zr(Cl)H or Cp$_2$ZrH$_2$. The reaction of a 1:1 mixture of 3a and 2-methylpropanal (3c) under the influence of Cp$_2$ZrH$_2$ at 20 °C for 0.5 h resulted in all possible esters, mixed cross-dimers 5 and 6, and homodimers 4a and 4c (eq 3) (Table III).

$$\text{3a} \ + \ \text{3c} \quad \xrightarrow[\text{20°C, 0.5 h under Ar}]{\text{Cp}_2\text{ZrH}_2 \ (5 \ \text{mol\%})}$$

(3)
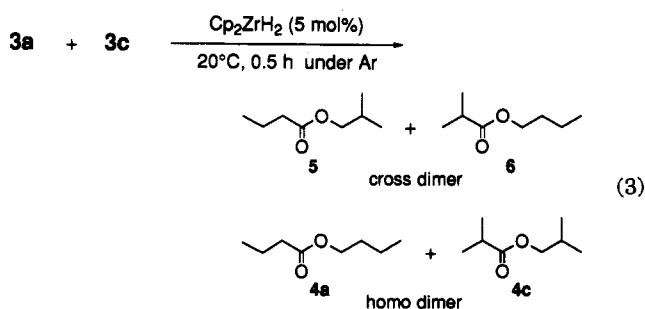
The hydrogenation of aldehydes 3a and 3c was accompanied by an undesired reaction, especially in Cp$_2$ZrH$_2$, to form the corresponding alcohols. The Cp$_2$Zr(Cl)H catalyzed reaction afforded cross-dimer 5 in preference to alternative ester 6. The preferred formation of 5 shows that 3c is more easily added to the zirconocene complexes than 3a. Similar results were also obtained in the cross-dimerization of 3a with cyclohexanecarboxaldehyde (3f).

It is interesting to note that the cross-esterification of 3a with benzaldehyde (3g) was smoothly catalyzed by both Cp$_2$Zr(Cl)H and Cp$_2$ZrH$_2$ complexes, despite the fact that the esterification of 3g itself was difficult under these conditions. It is particularly of interest that the cross-esterification of 3a with 3g proceeded in high selectivity to give benzyl butyrate (7) without formation of butyl benzoate (8) as the cross-dimer. In addition, the cross-dimer 7 was obtained in preference to the homo-dimer 4a. To explain this observation, it is considered that the insertion of 3g into the Zr-H bond occurs more easily than that of 3a. When a 1:2 mixture of 3a and 3g was allowed to react in the presence of Cp$_2$Zr(Cl)H, 7 was exclusively formed as the cross-dimer (eq 4).

$$\text{3a} \ + \ 2 \ \text{3g} \quad \xrightarrow[\text{20°C, 0.5 h under Ar}]{\text{Cp}_2\text{Zr(Cl)H} \ (5 \ \text{mol\%})}$$

cross dimer (54 %, 7 : 8 = 99 > 1)

(4)

4a + 4g

homo dimer (22 %, 4a : 4g = 99 : 1)

It is noteworthy that 7 was selectively produced from 3a and 3g by using the zirconocene complexes, because the cross-esterification of 3a and 3g using RuH$_2$(PPh$_3$)$_4$ affords the homo-dimer 4a in preference to the mixed dimers 7 and 8.[12]

In order to achieve the cross-dimerization of different kinds of aldehydes having similar reactivities, Cp$_2$Zr(Cl)H

Table III. Cross-Dimerization of Aldehydes Catalyzed by Cp$_2$ZrH$_2$ and Cp$_2$Zr(Cl)H[a]

aldehyde		catalyst	yield/mmol					
R^1–CHO	R^2–CHO		R^1–CO$_2$CH$_2$–R^2	R^2–CO$_2$CH$_2$–R^1	R^1–CO$_2$CH$_2$–R^1	R^2–CO$_2$CH$_2$–R^2	R^1–CH$_2$OH	R^2–CH$_2$OH
3a	3c	Cp$_2$ZrH$_2$	0.63	0.32	0.40	0.54	0.22	0.39
	3c	Cp$_2$Zr(Cl)H	0.58	0.29	0.40	0.48	0.13	0.20
	3f	Cp$_2$ZrH$_2$	0.63	0.22	0.24	0.56	0.20	0.49
	3f	Cp$_2$Zr(Cl)H	0.95	0.26	0.56	0.43	0.14	0.21
	3g	Cp$_2$ZrH$_2$	0.85	trace	0.56	0.04	0.14	0.52
	3g	Cp$_2$Zr(Cl)H	0.78	trace	0.64	0.03	0.07	0.13
	3g[b]	Cp$_2$ZrH$_2$	1.27	0.05	0.39	0.07	0.17	0.90
	3g[b]	Cp$_2$Zr(Cl)H	1.35	trace	0.49	0.06	0.07	0.36

[a] R^1–CHO (2.5 mmol) and R^2–CHO (2.5 mmol) were allowed to react with Cp$_2$ZrH$_2$ or Cp$_2$Zr(Cl)H (0.25 mmol, 5 mol %) at 20 °C for 0.5 h under Ar. [b] 3g (5.0 mmol) was used.

was allowed to stoichiometrically react with 3f followed by 3c. As expected, the cross-dimerization was successfully carried out to form cross-dimer 9 without the formation of the alternative cross-dimer 10, along with a small amount of homo-dimers 4c and 4f (eq 5).
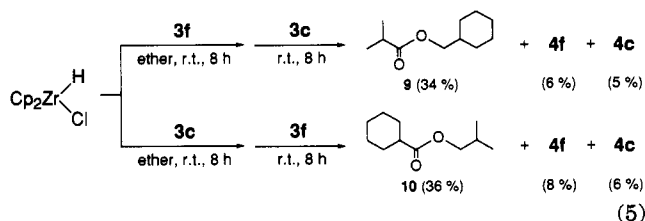
It was found that the initially used aldehyde 3f was introduced to the alcohol side of the ester. In contrast, 3c was allowed to react with Cp$_2$Zr(Cl)H followed by 3f to form cross-ester 10.

When bis(η^5-cyclopentadienyl)chlorozirconium deuteride, Cp$_2$Zr(Cl)D, was used in the cross-esterification of 3f with 3c, (cyclohexyl-1)methyl-d 2-methylpropanoate (11) in which deuterium is incorporated more than >98% was obtained in 35% yield (eq 6).
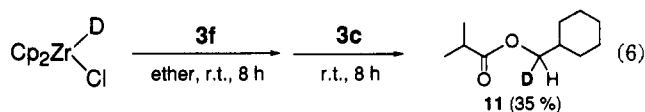

Reaction Path

To obtain the mechanistic information concerning the present esterification of aldehydes, zirconocene complexes Cp$_2$ZrH$_2$ and Cp$_2$Zr(Cl)H were allowed to react with 2 equiv of 2-methylpropanal (3c) at 0 °C for 0.5 h. During this reaction of the Cp$_2$ZrH$_2$ with 3c, no ester was formed, while in the reaction of the Cp$_2$Zr(Cl)H ester 4c was obtained in 36% yield. This observation suggests that two molecules of aldehyde are capable of being inserted into the Cp$_2$ZrH$_2$ to form Cp$_2$Zr(OCH$_2$R)$_2$, while only one molecule of aldehyde adds to Cp$_2$Zr(Cl)H to form Cp$_2$-Zr(Cl)OCH$_2$R.

NMR results are especially helpful for explaining the differences in selectivity in cross-esterification. The ^{1}H-NMR of a 1:1 mixture of Cp$_2$Zr(Cl)H and 3a or benzaldehyde (3g) gave a doublet at δ 3.6 due to a methylene proton or a singlet at δ 4.9 due to a methylene, which shows the formation of Cp$_2$Zr(Cl)OCH$_2$CH(CH$_3$)$_2$ (12) or Cp$_2$Zr(Cl)OCH$_2$Ph (13), respectively (Figure 1).

Furthermore, the ^{1}H-NMR of a mixture of Cp$_2$Zr(Cl)H and 3a (2 equiv) indicated the formation of 12 and ester

4a.[16] However, the ^{1}H-NMR spectrum of a mixture of Cp$_2$Zr(Cl)H and 3g (2 equiv) was found to consist of 13 and the unreacted 3g,[17] but no peak signifying ester 4g was observed. The former observation indicates that the migration of the 2-methylpropoxy moiety from the resulting complex 12 to a second aldehyde occurs smoothly to form the ester 4a via an intermediate [B], as discussed later. In contrast to the reaction with the aliphatic aldehyde 3a, the reaction of Cp$_2$Zr(Cl)H with aromatic aldehyde 3g stopped at the formation stage of 13 without the production of the ester 4g, and the 3g remaining was recovered unaltered. This fact shows that the migation of the benzyloxy moiety from complex 13 to a second 3g is difficult to take place. However, it was found that the reaction of complex 13 with an aliphatic aldehyde such as 3a produced cross-ester 7 (22%) together with 4a (20%) after quenching with water (eq 7).
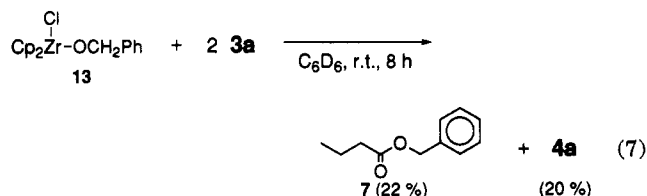
We are therefore forced to assume that the coordination of the aromatic aldehyde 3g to complex 13 takes place with more difficulty than that of the aliphatic aldehyde 3a to 13 probably because of the lower electron density of the carbonyl oxygen of 3g based on the electron-withdrawing property of the phenyl group.

On the basis of the these results, the following route is suggested for the present catalytic conversion of aldehyde into ester using Cp$_2$Zr(Cl)H (Scheme I).

The aldehyde inserts into the Zr–H bond to form an alkoxyzirconium species [A] which is the key intermediate in the present reaction. The second molecule of aldehyde coordinates to complex A, followed by the migratory insertion of the aldehyde to form complex B. The third aldehyde molecule coordinates to intermediate B on which a subsequent hydrogen transfer reaction to the third aldehyde via a six-membered transition state C produces the ester, while complex A is regenerated. However, the higher activity of the sterically crowded aldehydes such as 3e and 3f compared to that of the linear aldehydes such as 3a and 3b may suggest a reaction sequence which involves a direct β-hydride elimination from the inter-

(16) Complex 12 was treated with ether containing water to give 2-methylpropanol and 4a in 50% and 36% yields, respectively, based on 3a used.

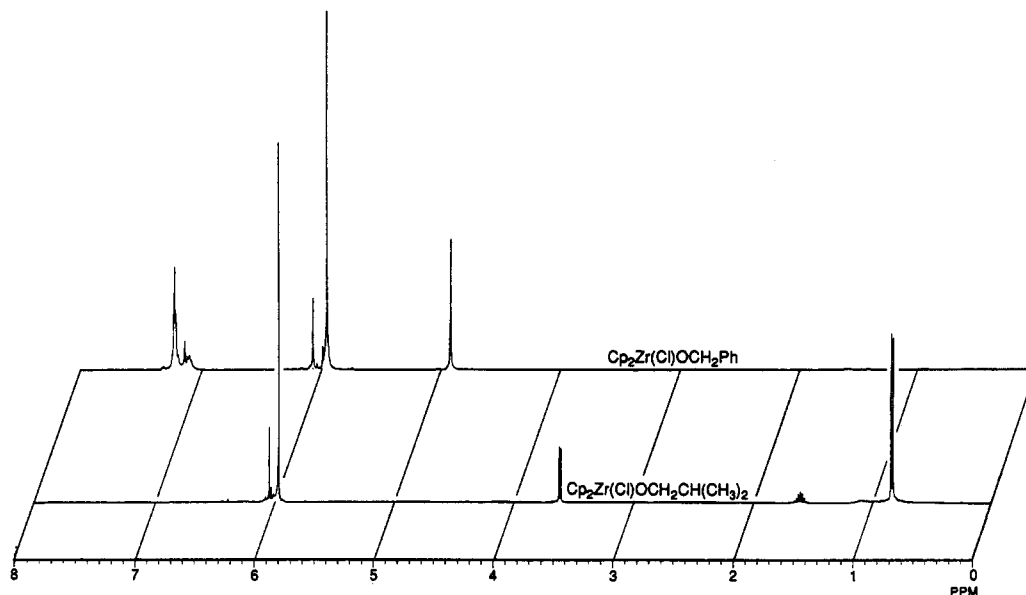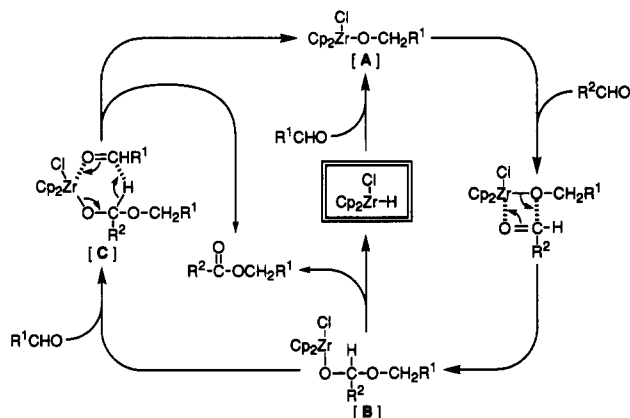(17) Treatment of complex 13 similar to that of ref 16 afforded benzyl alcohol (49%) and 3g (42%).

Figure 1. ^{1}H-NMR spectra of $Cp_2Zr(Cl)OCH_2CH(CH_3)_2$ (**12**) and $Cp_2Zr(Cl)OCH_2Ph$ (**13**).

Scheme I. Conceivable Reaction Path for Dimerization of Aldehyde to Ester Catalyzed by $Cp_2Zr(Cl)H$

mediate **B** releasing the ester and regenerating the Cp_2-$Zr(Cl)H$. Unfortunately, if the reaction of an aldehyde with $Cp_2Zr(Cl)H$ progresses more easily than that with $Cp_2Zr(Cl)OCH_2R$ [**A**], $Cp_2Zr(Cl)H$ is difficult to observed in the NMR study even though the $Cp_2Zr(Cl)H$ is regenerated by the β-hydride elimination from complex **B**. Therefore, we are unable to determine whether the reaction proceeds *via* the six-membered transition state **C** or the direct β-hydride elimination from **B** in the reaction sequence shown in Scheme I.

In the Cp_2ZrH_2 catalyzed esterification of aldehyde, it is probable that the reaction proceeds *via* the dialkoxy-zirconium complex such as $Cp_2Zr(OR)_2$ rather than the monoalkoxy complex such as $Cp_2Zr(H)OR$, because two molecules of aldehyde insert very readily into the Zr–H bond. Indeed, the reaction of Cp_2ZrH_2 with 2 equiv of **3c** produced no ester, as previously mentioned.

In conclusion, we have presented the selective dimerization of aldehydes catalyzed by zirconocene and hafnocene complexes. It is noteworthy that the cross-esterification between benzaldehyde (**3g**) and various aldehydes was achieved with high selectivity, despite the fact that the esterification of **3g** itself was difficult to carry out using the present catalytic systems.

Experimental Section

All reactions and manipulations were carried out under argon using flame dried Schlenk tubes. Solvents were dried and purified in the usual manner and stored under an argon atmosphere. Commercial aldehydes were freshly distilled over 4-Å molecular sieves. The reaction products were quantitatively analyzed by GLC using an internal standard. GLC was performed using a PEG (25-m) column. IR spectra were recorded on a FT-IR spectrometer. ^{1}H- and ^{13}C-NMR spectra were obtained on a 400-MHz spectrometer.

Preparation of Group 4 Metallocene Complexes. Cp_2ZrCl_2, $Cp_2Zr(Cl)H$, and Cp_2ZrH_2 were prepared according to conventional methods.[18,19] The low valent zirconocene complex, Cp_2Zr, was obtained by adding *n*-BuLi (1.6 mol/L hexane solution, 0.31 mL) to a solution of Cp_2ZrCl_2 (0.073 g, 0.25 mmol) in anhydrous THF (0.5 mL) at 0 °C, followed by solvent removal *in vacuo*.[20] Various hafnocene complexes were prepared by a procedure similar to the corresponding zirconocene complexes. $Cp_2Zr(Cl)D$ was obtained by using $LiAlD_4$ instead of $LiAlH_4$ during the preparation of the corresponding hydride complex.

Cp_2ZrCl_2: IR (KBr) 3105, 1440, 1015, 810 cm^{-1}.
$Cp_2Zr(Cl)H$: IR (KBr) 3095, 1460, 1390, 1010, 810 cm^{-1}.
Cp_2ZrH_2: IR (KBr) 3070, 1525, 1330, 1015, 805 cm^{-1}.
Cp_2HfCl_2: IR (KBr) 3105, 1440, 1015, 815 cm^{-1}.
$Cp_2Hf(Cl)H$: IR (KBr) 3100, 1460, 1390, 1015, 810 cm^{-1}.
Cp_2HfH_2: IR (KBr) 3070, 1570, 1380, 1015, 810 cm^{-1}.
$Cp_2Zr(Cl)D$: IR (KBr) 3095, 1440, 1025, 1010, 810 cm^{-1}.

General Procedure for Dimerization of Aldehydes Catalyzed by Group 4 Metallocene Complexes. Into the Schlenk tube containing Cp_2ZrH_2 (0.056 g, 0.25 mmol), freshly distilled 3-cyclohexene-1-carboxaldehyde (**1**) (0.55 g, 5 mmol) was added at 0 °C under the argon atmosphere. The reaction mixture was stirred at 0 °C for 0.5 h. GLC analysis of the resulting yellow solution indicated the presence of (3-cyclohexenyl)methyl 3-cyclohexene-1-carboxylate (**2**) and a small amount of 3-cyclohexenemethanol. Reactions of other aldehydes were carried out using the previously described method.

General Procedure for Cross-Dimerization of Aldehydes Catalyzed by Cp_2MH_2 and $Cp_2M(Cl)H$ (M = Zr or Hf). Into the Schlenk tube containing catalyst (0.25 mmol) were added at 0 °C a mixture of freshly distilled butanal (**3a**) (0.180 g, 2.5 mmol) and 2-methylpropanal (**3c**) (0.180 g, 2.5 mmol). The reaction mixture was stirred at 20 °C for 0.5 h under an argon atmosphere.

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(19) Wailes, P. C.; Weigold, H. *Inorg. Synth.* **1979**, *19*, 223.
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From GLC analysis of the resulting yellow solution, all possible esters **4a, 4c, 5** and **6** were observed accompanied by small amounts of 1-butanol and 2-methyl-1-propanol. Cross-dimerization of other aldehydes were similarly carried out.

Stoichiometric Cross-Dimerization of Cyclohexanecarboxaldehyde (3f) with 2-Methylpropanal (3c). Into the Schlenk tube containing Cp₂Zr(Cl)H (0.258 g, 1 mmol) in ether (1 mL) was added **3f** (0.112 g, 1 mmol), and the mixture was stirred at 20 °C for 8 h. To the resulting solution was added **3c** (0.072 g, 1 mmol), and the solution was further stirred for 8 h to provide a yellow suspended solution. GLC analysis of the solution indicated the presence of the cross-dimer, 1-cyclohexylmethyl 2-methylpropanoate (**9**), and homo-dimers.

Reaction of 2-Methylpropanal (3c) with Cp₂Zr(Cl)H or Cp₂ZrH₂. Into the Schlenk tube containing the zirconocene complex (1 mmol) in ether (1 mL) was added **3c** (0.144 g, 2 mmol), and the mixture was stirred at 20 °C for 8 h. In the case of the Cp₂Zr(Cl)H, GLC analysis of the reactant indicated the presence of the corresponding ester **4c**, while from the reaction with Cp₂-ZrH₂, no ester was observed.

Cross-Dimerization of Cp₂Zr(Cl)D with Cyclohexanecarboxaldehyde (3f) and 2-Methylpropanal (3c). Into the Schlenk tube containing Cp₂Zr(Cl)D (0.259 g, 1 mmol) in ether (1 mL) was added **3f** (0.112 g, 1 mmol), and the mixture was stirred at 20 °C for 8 h. To the resulting solution was added **3c** (0.072 g, 1 mmol), and the solution was further stirred for 8 h to provide a yellow suspended solution. ¹H- and ¹³C-NMR spectra indicated the presence of an ester incorporated deuterium, (cyclohexyl-1)methyl-*d* 2-methylpropanoate (**11**).

NMR Study of the Reaction of Cp₂Zr(Cl)H with Aldehydes. Into the Schlenk tube containing Cp₂Zr(Cl)H (0.258 g, 1 mmol) in C₆D₆ (1 mL) was added 2-methylpropanal (**3c**) (0.072 g, 1 mmol) or benzaldehyde (**3g**) (0.106 g, 1 mmol). Stirring the reaction mixture at 20 °C for 8 h under an argon atmosphere provided complex **12** or **13**, respectively. ¹H- and ¹³C-NMR spectra were measured intact under an argon atmosphere.

Cp₂Zr(Cl)OCH₂CH(CH₃)₂ (12): ¹H-NMR (C₆D₆/Me₄Si) δ 5.96 (s, 10H), 3.60 (d, 2H), 1.60 (sept, 1H), 2.83 (6H); ¹³C-NMR (C₆D₆/Me₄Si) δ 113.4, 82.5, 32.0, 19.2.

Cp₂Zr(Cl)OCH₂Ph (13): ¹H-NMR (C₆D₆/Me₄Si) δ 7.24–7.10 (m, 5H), 5.94 (s, 10H), 4.89 (s, 2H); ¹³C-NMR (C₆D₆/Me₄Si) δ 142.5, 128.6, 127.3, 126.6, 113.7, 77.2.

Spectral Data

(3-Cyclohexenyl)methyl 3-Cyclohexene-1-carboxylate (2): IR (NaCl) 3025, 2920, 2840, 1735, 1440, 1305, 1220, 1165, 1015, 655 cm⁻¹; ¹H-NMR (CDCl₃/Me₄Si) δ 5.68 (m, 4H), 4.00 (d, 2H), 2.57 (m, 1H), 2.27–1.95 (m, 8H), 1.81–1.64 (m, 3H), 1.38–1.27 (m, 1H); ¹³C-NMR (CDCl₃/Me₄Si) δ 175.9, 127.1, 126.7, 125.6, 125.3, 68.6, 39.5, 33.1, 28.2, 27.5, 25.3, 25.1, 24.5.

1-Butyl 1-butanoate (4a): IR (NaCl) 2965, 2875, 1740, 1460, 1255, 1180, 1093 cm⁻¹; ¹H-NMR (CDCl₃/Me₄Si) δ 4.08 (t, 2H), 2.28 (t, 2H), 1.68 (m, 4H), 1.38 (sext, 2H), 0.95 (t, 3H), 0.94 (t, 3H); ¹³C-NMR (CDCl₃/Me₄Si) δ 173.9, 64.1, 36.3, 30.7, 19.2, 18.5, 13.8, 13.7.

1-Hexyl 1-hexanoate (4b): IR (NaCl) 2958, 2932, 2861, 1738, 1466, 1245, 1174, 1111, 999, 729 cm⁻¹; ¹H-NMR (CDCl₃/Me₄Si) δ 4.06 (t, 2H), 2.29 (t, 2H), 1.67–1.58 (m, 4H), 1.38–1.24 (m, 10H), 0.91–0.87 (m, 6H); ¹³C-NMR (CDCl₃/Me₄Si) δ 174.0, 64.4, 34.4, 31.4, 31.3, 28.6, 25.6, 24.7, 22.5, 22.3, 14.0, 13.9.

2-Methyl-1-propyl 2-methylpropanoate (4c): IR (NaCl) 2970, 2880, 1740, 1470, 1385, 1260, 1195, 1155, 1075 cm⁻¹; ¹H-NMR (CDCl₃/Me₄Si) δ 3.85 (d, 2H), 2.56 (sept, 1H), 1.94 (sept, 1H), 1.18 (d, 6H), 0.94 (d, 6H); ¹³C-NMR (CDCl₃/Me₄Si) δ 177.0, 70.2, 34.0, 27.7, 19.0, 18.9.

2-Methyl-1-pentyl 2-methylpentanoate (4d): IR (NaCl) 2961, 2934, 2874, 1736, 1465, 1379, 1246, 1181, 1149, 1085, 984, 741 cm⁻¹. ¹H-NMR (CDCl₃/Me₄Si) δ 3.98–3.92 (m, 1H), 3.89–3.83 (m, 1H), 2.45 (sext, 1H), 1.83–1.62 (m, 1H), 1.46–1.25 (m, 8H), 1.14 (d, 3H), 0.93–0.88 (m, 9H). ¹³C-NMR (CDCl₃/Me₄Si) δ 177.0, 69.1, 39.5, 39.4, 36.0, 35.7, 32.4, 20.4, 19.9, 17.1, 16.9, 16.8, 14.2, 14.0.

2,2-Dimethyl-1-propyl 2,2-dimethylpropanoate (4e): IR (NaCl) 2961, 2907, 2873, 1733, 1480, 1366, 1286, 1159, 988 cm⁻¹; ¹H-NMR (CDCl₃/Me₄Si) δ 3.75 (s, 2H), 1.22 (s, 9H), 0.95 (s, 9H); ¹³C-NMR (CDCl₃/Me₄Si) δ 178.5, 73.6, 38.9, 31.5, 27.3, 26.4.

1-Cyclohexylmethyl cyclohexanecarboxylate (4f): IR (NaCl) 2930, 2855, 1730, 1450, 1310, 1245, 1170, 1135, 1035 cm⁻¹. ¹H-NMR (CDCl₃/Me₄Si) δ 3.86 (d, 2H), 2.33–2.25 (m, 1H), 1.92–1.88 (m, 2H), 1.74–1.57 (m, 9H), 1.48–1.39 (m, 2H), 1.33–1.11 (m, 6H), 1.01–0.92 (m, 2H). ¹³C-NMR (CDCl₃/Me₄Si) δ 176.2, 69.3, 43.4, 37.2, 29.9, 29.1, 26.4, 25.8, 25.7, 25.5.

Benzyl benzoate (4g): IR (NaCl) 1720, 1452, 1376, 1314, 1272, 1110, 1070, 1026, 751, 712 cm⁻¹; ¹H-NMR (CDCl₃/Me₄Si) δ 8.08 (d, 2H), 7.56 (t, 1H), 7.46–7.32 (m, 7H), 5.37 (s, 2H); ¹³C-NMR (CDCl₃/Me₄Si) δ 166.4, 136.0, 133.0, 130.1, 129.7, 128.6, 128.4, 128.2, 128.1, 66.7.

2-Methyl-1-propyl 1-butanoate (5): IR (NaCl) 2965, 2875, 1740, 1470, 1380, 1179, 1000, 755 cm⁻¹; ¹H-NMR (CDCl₃/Me₄Si) δ 3.86 (d, 2H), 2.30 (t, 2H), 1.93 (sept, 1H), 1.66 (sext, 2H), 0.95 (t, 3H), 0.93 (d, 6H); ¹³C-NMR (CDCl₃/Me₄Si) δ 173.8, 70.4, 36.3, 27.7, 19.1, 18.5, 13.7.

1-Butyl 2-methylpropanoate (6): IR (NaCl) 2964, 2936, 2876, 1737, 1470, 1390, 1345, 1193, 1159, 1078, 972 cm⁻¹; ¹H-NMR (CDCl₃/Me₄Si) δ 4.07 (t, 2H), 2.54 (sept, 1H), 1.61 (hept, 2H), 1.38 (sext, 2H), 1.16 (d, 6H), 0.94 (t, 3H); ¹³C-NMR (CDCl₃/Me₄Si) δ 177.6, 64.4, 34.3, 31.0, 19.4, 19.3, 14.0.

Benzyl 1-butanoate (7): IR (NaCl) 3035, 2965, 2875, 1735, 1455, 1255, 1170, 1090, 975, 750, 700 cm⁻¹; ¹H-NMR (CDCl₃/Me₄Si) δ 7.36–7.32 (m, 5H), 5.12 (s, 2H), 2.34 (t, 2H), 1.67 (sext, 2H), 0.95 (t, 3H); ¹³C-NMR (CDCl₃/Me₄Si) δ 173.5, 136.2, 128.6, 128.2, 66.1, 36.2, 18.5, 13.7.

1-Butyl benzoate (8): IR (NaCl) 2960, 2874, 1720, 1602, 1452, 1385, 1314, 1276, 1176, 1112, 1070, 1027, 711 cm⁻¹; ¹H-NMR (CDCl₃/Me₄Si) δ 8.05 (d, 2H), 7.55 (t, 1H), 7.44 (t, 2H), 4.33 (t, 2H), 1.76 (hept, 2H), 1.48 (sext, 2H), 0.98 (t, 3H); ¹³C-NMR (CDCl₃/Me₄Si) δ 166.7, 132.8, 130.5, 129.5, 128.3, 64.8, 30.7, 19.3, 13.7.

1-Cyclohexylmethyl 2-methylpropanoate (9): IR (NaCl) 2974, 2929, 2854, 1737, 1470, 1451, 1391, 1344, 1261, 1194, 1156, 1076, 991, 756 cm⁻¹. ¹H-NMR (CDCl₃/Me₄Si) δ 3.87 (d, 2H), 2.55 (sept, 1H), 1.75–1.58 (m, 7H), 1.31–1.10 (m, 8H), 1.01–0.95 (m, 2H); ¹³C-NMR (CDCl₃/Me₄Si) δ 177.3, 69.4, 37.2, 34.1, 29.7, 26.4, 25.7, 19.1.

2-Methyl-1-propyl cyclohexanecarboxylate (10): IR (NaCl) 2934, 2857, 1733, 1469, 1451, 1380, 1313, 1247, 1171, 1133, 1039, 992, 756 cm⁻¹. ¹H-NMR (CDCl₃/Me₄Si) δ 3.84 (d, 2H), 2.30 (tt, 1H), 1.94–1.89 (m, 3H), 1.76–1.73 (m, 3H), 1.49–1.40 (m, 2H), 1.33–1.18 (m, 3H), 0.93 (d, 6H); ¹³C-NMR (CDCl₃/Me₄Si) δ 176.2, 70.2, 43.3, 29.1, 27.8, 25.8, 25.5, 19.1.

(Cyclohexyl-1)methyl-*d* 2-methylpropanoate (11): ¹H-NMR (CDCl₃/Me₄Si) δ 3.86–3.84 (m, 1H), 2.55 (sept, 1H), 1.75–1.60 (m, 7H), 1.29–1.14 (m, 8H), 1.01–0.92 (m, 2H); ¹³C-NMR (CDCl₃/Me₄Si) δ 177.3, 69.1 (t), 37.1, 34.1, 29.7, 29.6, 26.4, 25.7, 19.1.