Accounts

Ruthenium Complex-catalyzed Highly Selective Co-oligomerization of Alkenes[†]

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Ruthenium complex-catalyzed reactions often require highly qualified tuning of reaction conditions with substrates to attain high yield and selectivity of the products. In this review, our strategies for achieving characteristic ruthenium complex-catalyzed co-oligomerization of different alkenes are disclosed: 1) The codimerization of 2-norbornenes with acrylic compounds by new ruthenium catalyst systems of $RuCl_3$(tpy)/Zn [tpy = 2,2':6',2''-terpyridine] or $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$/Zn in alcohols, 2) A novel synthesis of 2-alkylidenetetrahydrofurans from dihydrofurans and acrylates by zerovalent ruthenium catalysts, such as $Ru(\eta^4\text{-cod})(\eta^6\text{-cot})$ [cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene] and $Ru(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ [dmfm = dimethyl fumarate], 3) Regio- and stereoselective synthesis of enamides by $Ru(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$-catalyzed codimerization of *N*-vinylamides with alkenes, and 4) Unusual *head-to-head* dimerization of styrenes and linear codimerization of styrenes with ethylene by $Ru(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ catalyst in the presence of primary alcohols.

Key Words : Ruthenium, Catalyst, Co-oligomerization, Alkenes, Atom-efficiency

Introduction

Alkenes are key materials in the petrochemical industry.[1] They are easily available, cheap, reactive, and readily converted into a range of valuable chemicals.[2] Catalytic dimerization, codimerization, and co-oligomerization of alkenes are one of the most important methodologies in organic synthesis directed toward a green and sustainable chemistry, since in these reactions all the atoms of the starting materials are incorporated into the products without generation of wastes (100% atom-economy).[3] Dimerization and codimerization have been widely used on an industrial scale, and provide a variety of biodegradable detergents, new kinds of polymers, lubricants, and many other industrially useful chemicals.[4]

The first simple alkene dimerization was discovered in the course of Ziegler's study on catalytic oligomerization of ethylene to long-chain terminal alkenes by using alkylaluminum compounds.[5] This discovery led to the invention of the Ziegler catalysts[6] for polymerization, hydrogenation,

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isomerization as well as metathesis of alkenes, and this chemistry provides the basis for the Shell Higher Olefins process (SHOP).[7] In addition, these reactions served as good models for the study of the characterization and reactivity of metal-carbon bonds.[8] For example, the polymerization mechanism is illustrated as a polyinsertion of alkenes into hydrido- and carbon-metal bonds. Dimerization can be also explained using this model, where the rate of β-hydrogen abstraction is faster than that of polyinsertion of alkenes.

Codimerization of styrenes with ethylene, so-called hydrovinylation, has been much studied since its first report by Alderson and coworkers with RhCl$_3$ and RuCl$_3$ catalysts in 1965.[9] Many transition metal complexes are applicable for this process[10,11] and among them, nickel catalysts are most active.[12] The main products are branched (head-to-tail) codimers, 3-aryl-1-butenes, and the enantioselective version has recently been developed.[13,14] In addition to styrene, a variety of alkenes, such as 2-norbornene,[15] vinyl acetate,[16] and indene,[16] are employed in this hydrovinylation. Recently, an iridium-siloxide[17] and a bis(indenyl)yttrium hydride[18] have been synthesized and fully characterized to establish the mechanism of catalytic codimerization of styrenes with alkenes. Both stoichiometric and catalytic codimerization of butenes with ethylene by using a dicationic Pt(II)-ethylene complex have also been investigated in detail.[19]

In 1976, Mitsudo and coworkers first used ruthenium complexes as an effective catalyst for [2 + 2] cycloaddition of 2-norbornenes with alkynes.[20] This chemistry has been extended to linear codimerization of alkynes with 1,3-dienes[21] and acrylic compounds,[22] as well as unusual dimerization of 2,5-norbornadiene to pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-diene, PCTD, via C-C bond cleavage.[23] In 1995, Murai and Trost independently developed chelation-assisted codimerization of α,β-enones with vinylsilanes[24] catalyzed by a ruthenium complex, RuH$_2$(CO)(PPh$_3$)$_3$, which is also an efficient catalyst for aromatic C-H/alkene coupling reactions.[25] Subsequently, Murai and coworkers reported the codimerization of acyclic α,β-enones with alkenes.[26] Kim and coworkers reported rhodium-catalyzed codimerization of 2-vinylpyridines with alkenes.[27]

However, there have been relatively few reported examples of transition metal complex-catalyzed chemo-, regio-, and stereoselective codimerization and co-oligomerization of functionalized alkenes, which give synthetically and industrially important polyfunctionalized monomers.

In this review, discussion will be focused on the recent progress of ruthenium-catalyzed co-oligomerization of different alkenes, developed mainly by the present authors.[28]

Ruthenium Complex-catalyzed Regio- and Stereoselec- tive Linear Codimerization of 2-Norbornenes with Acrylic Compounds.[29] Linear codimerization of unsaturated hydrocarbons affording valuable chemicals has been receiving considerable attention from industrial aspects.[4] Hydrovinylation of alkenes and dienes (addition of *ethylene* to alkenes and dienes) which originated from the research by Alderson and coworkers appeared in 1965 in the open literature.[9] This is one of the most successfully developed reactions among the codimerizations so far reported, and is known to be preeminently catalyzed by several late transition metal complexes, such as Ni and Pd, with high enantioselectivity.[13,14] On the other hand, although linear codimerization of alkenes and/or dienes except hydrovinylation also has been intensively investigated, the scope of substrates is still rather limited, and most of the reactions suffer from difficulty in controlling the dimerization selectivity as well as the regio- and stereoselectivity.[9,24,26,30] In the course of our investigation on the low-valent ruthenium-catalyzed selective dimerization reactions of unsaturated hydrocarbons,[20-23] we found a linear codimerization of a novel combination of substrates, 2-norbornenes and acrylic compounds. The reaction proceeds regio- and stereoselectively by ruthenium catalyst systems involving neutral tridentate ligands, RuCl$_3$-(tpy) (tpy = 2,2':6',2"-terpyridine) (**1**) or [RuCl$_2$(η^6-C$_6$H$_6$)]$_2$ (**3**), in the presence of Zn in an alcoholic solvent.

First, complex **1**, which can be reduced by an appropriate reductant to generate electron-rich low-valent species in situ, was used as a catalyst. The reaction of 2-norbornene (5.0 mmol) with methyl acrylate (1.0 mmol) in the presence of 5 mol% of complex **1** and Zn powder (0.50 mmol) in MeOH under reflux for 1 h gave a corresponding *exo-trans* codimer, **2a**, as a major product (Scheme 1).

Catalytic activity of several ruthenium and group 9 metal complexes in the presence of Zn was surveyed in the codimerization of 2-norbornene with methyl acrylate. Complex **1** gave the best result (87% yield, *trans*:*cis* ratio > 40:1) among ruthenium polypyridyl complexes (RuCl$_3$(tbtpy) [tbtpy = 4,4',4"-tri-tert-butyl-2,2':6',2"-terpyridine]: **2a**, 8%, and RuCl$_4$(bpy) [bpy = 2,2'-bipyridine]: **2a**, 20%). In the absence of Zn, **1** did not show catalytic activity. In place of **1**, RuCl$_2$(PPh$_3$)$_3$ showed some catalytic activity (**2a**, 20%), whereas [RuCl$_2$(CO)$_3$]$_2$ was totally ineffective. [RuCl$_2$(η^6-C$_6$H$_6$)]$_2$ (**3**) was found to be also effective, and the activity is comparable to that of **1** (87% yield, *trans*:*cis* ratio = 12:1). However, other η^6-substituted arene complexes such as [RuCl$_2$(η^6-*p*-cymene)]$_2$ and [RuCl$_2$(η^6-C$_6$Me$_6$)]$_2$ were not efficient. No dissociation of these arenes was observed by the careful GC-MS analysis, indicating that the arenes stay on ruthenium and work as spectator ligands. Thus, the bulky

exo-trans-**2a**
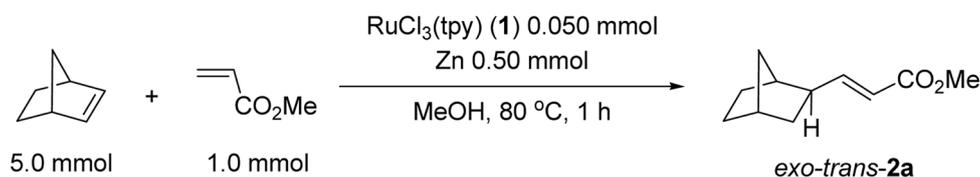
Scheme 1

arene ligands seem to lower the catalytic activity by steric hindrance against the substrates. Catalytic activity of RuH$_2$-(PPh$_3$)$_4$, Ru(η^4-cod)(η^6-cot) [cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene] and Ru(CO)$_3$(PPh$_3$)$_2$, which are zero-valent or can be easily reduced to zero-valent in situ, was examined without Zn, and the former two complexes were somewhat effective (up to 26% yield), but the latter was almost ineffective. Rhodium and iridium complexes bearing a tpy ligand showed no catalytic activity.

Several metals were examined as reducing agents instead of Zn under the same reaction conditions as shown in Scheme 1. A Zn-Cu couple gave the codimers in 75% yield, whereas others such as Al, Fe, and Mg afforded **2a** in 7, 4, and 0% yield, respectively. When sodium and potassium carbonates were used in place of Zn, only trace amounts of the codimers were obtained.

The effect of solvents was also found to be critical in the **1**/Zn-catalyzed codimerization. MeOH was the best solvent

Table 1. Ruthenium complex-catalyzed linear codimerization of 2-norbornenes with acrylic compounds[a]

entry	substrates		products		reaction conditions	yield (%) (*trans:cis*)[b]
	2-norbornenes	acrylic compounds				
1		⟍⟍CO$_2$Me	⟍⟍CO$_2$Me	**2a**	MeOH 80°C, 1 h	80 (> 40 : 1)
2		⟍⟍CO$_2$Et	⟍⟍CO$_2$Et	**2b**	EtOH 90°C, 1 h	82 (20 : 1)
3		⟍⟍CO$_2^n$Pr	⟍⟍CO$_2^n$Pr	**2c**	*n*-PrOH 100 °C, 1h	62 (20 : 1)
4		⟍⟍CO$_2^n$Bu	⟍⟍CO$_2^n$Bu	**2d**	*n*-BuOH 100°C, 1 h	76 (8.5 : 1)
5		⟍⟍CO$_2^t$Bu	⟍⟍CO$_2^t$Bu	**2e**	*n*-BuOH 100°C, 1 h	62 (11 : 1)
6[c]		⟍⟍CO$_2$Cy	⟍⟍CO$_2$Cy	**2f**	*i*-PrOH 90°C, 6 h	75 (12 : 1)
7		acrylate O/CH$_2$CH$_2$OMe	⟍⟍C(O)O–CH$_2$CH$_2$–O–Me	**2g**	*i*-PrOH 90°C, 4 h	52 (16 : 1)
8		acrylate O–CH$_2$CF$_3$	⟍⟍C(O)O–CH$_2$CF$_3$	**2h**	*i*-PrOH 90°C, 1 h	44 (10 : 1)
9[d]		⟍⟍CONMe$_2$	⟍⟍CONMe$_2$	**2i**	*i*-PrOH 80°C, 24 h	45 (8 : 1)
10[d]	norbornene-CO$_2$Me / CO$_2$Me	⟍⟍CO$_2$Me	product-CO$_2$Me/CO$_2$Me ⟍⟍CO$_2$Me	**2j**	*i*-PrOH 80°C, 24 h	45 (10 : 1)
11[d]	N-Me imide norbornene	⟍⟍CO$_2$Me	product ⟍⟍CO$_2$Me	**2k**	*i*-PrOH 80°C, 24 h	66 (5.6 : 1)
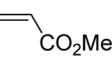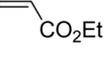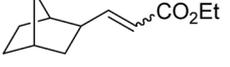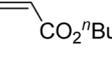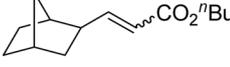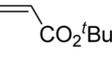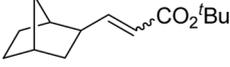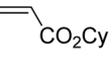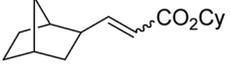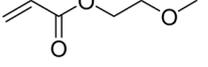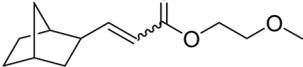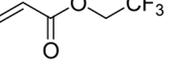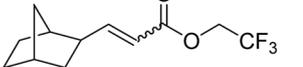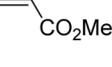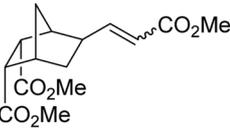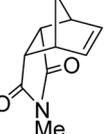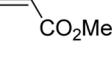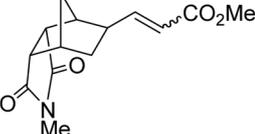
[a]2-Norbornenes (5.0 mmol), acrylic compounds (1.0 mmol), **1** (0.050 mmol), Zn (0.50 mmol). [b]Determined by GLC. [c]Cy = *cyclo*-C$_6$H$_{11}$. [d]**3** (0.025 mmol) was used instead of **1**.

(**2a**, 87%), while in a secondary alcohol, *i*-PrOH, the reaction was rather slow at 80 °C, and the yield of the product was 28% after 1 h. In *t*-BuOH or non-alcoholic solvents, such as toluene and THF, the codimerization did not proceed at all, probably because no reduction of the ruthenium species occurred in these solvents.

The **1** or **3**-catalyzed linear codimerization was applied to diverse substrates (Table 1). By the use of ethyl acrylate in EtOH, the *exo* codimers were obtained in 82% total yield with the *trans*:*cis* ratio of 20:1 (entry 2). Other acrylates having primary, secondary, and tertiary hydrocarbyl substituents in the ester moiety afforded the corresponding *exo-trans* and *cis* codimers in good yields, respectively (entries 3-6). Acrylates with heteroatom(s) in the ester moiety are also applicable (entries 7 and 8). In the case of *N,N*-dimethyl acrylamide, however, **1** could not catalyze the codimerization. Instead, **3** worked as a catalyst moderately to afford the codimers **2i** (entry 9). Substituted 2-norbornenes also reacted with methyl acrylate in the presence of **3** (entries 10 and 11). The scope of the catalytic activity of **3** seems to be wider than that of **1**. Reactions with unsymmetrical norbornene derivatives, such as dicyclopentadiene, and 5-vinyl-2-norbornene, gave a complex mixture. While *N*-methyl-7-oxa-5-norbornene-2,3-dicarboximide as a heteroatom bridged norbornene and benzonorbornadiene were also employed in the reaction with methyl acrylate; however, no conversion of the substrates was observed. The use of other electron-deficient alkenes such as acrylonitrile and vinyl ketones resulted in vain.

In Table 1, the results under various reaction conditions were summarized. EtOH, *n*-PrOH, *i*-PrOH and *n*-BuOH were used instead of MeOH (entries 2-8) to avoid the transesterification reaction. In entries 9-11, *i*-PrOH seems to be better than MeOH for the **3**/Zn catalyst system. When these reactions were conducted in MeOH, the yields of the corresponding codimers **2i**, **2j**, and **2k** were reduced to 18%, 6%, and 52%, respectively. As for the reaction temperature, for example, the reactions at 80 °C were also examined, but the yields were lower than those shown in entries 2-4, Table 1 (78%, 53%, and 44%, respectively). Thus, in some cases, higher reaction temperature is required to obtain the products in higher yields.

In order to elucidate a possible mechanism, a zero-valent ruthenium complex having a benzene ligand, Ru(η^6-C$_6$H$_6$)-(methyl acrylate)$_2$ (**4**), was examined as a catalyst, which is known to catalyze the homodimerization of methyl acrylate

in the presence of sodium naphthalenide.[31] Complex **4** was prepared by treatment of **3** with methyl acrylate and Zn in MeOH. 2-Norbornene reacted with *n*-butyl acrylate in the presence of 5 mol% of **4** in *n*-BuOH at 130 °C, affording the codimer **2d** in 79% (Scheme 2).

Moreover, the codimerization proceeded smoothly even in an aprotic solvent, such as *N,N*-dimethylacetamide (DMA), and diglyme. This suggests that in the **1** or **3**/Zn catalyst systems, an alcohol is not necessarily required as a solvent for the codimerization process, but is needed at the initial reduction step of ruthenium by Zn.

Two possible reaction pathways for the linear codimerization of 2-norbornene with an acrylate are illustrated in Scheme 3. In *path* A, coordination of 2-norbornene and an acrylate to an active zero-valent ruthenium species **5**, followed by oxidative cyclization gives a ruthenacyclopentane intermediate **6**. *β*-Hydrogen elimination to form **7** and successive reductive elimination would give **2** along with the regeneration of **5**. This metallacycle mechanism is proposed in the Fe(CO)$_5$-mediated photo-assisted reaction.[32] In addition, the *β*-hydrogen elimination from the ruthenacyclopentane (**6**→**7**) is supported by a DFT calculation (the energy barrier for the *β*-hydrogen elimination from non-substituted ruthenacyclopentane with a benzene ligand is estimated at 2.7 kcal/mol).[33] On the other hand, in *path* B, a ruthenium hydride species **8** is generated in situ initially, and 2-norbornene inserts into the Ru-H bond of **8** to give **9**. Subsequent insertion of acrylate into the Ru-C bond affords **10**. *β*-Hydrogen elimination from **10** would give **2** and a ruthenium hydride species **8** again. The mechanism involving successive insertion of alkenes *via* a metal hydride species has been well investigated by Brookhart and coworkers in the homodimerization of alkenes catalyzed by Rh and Pd.[34] The results using aprotic solvents shown in Scheme 2 indicate that the hydride in **8** should be derived from the acrylate, if the reaction proceeds *via path* B. As another mechanism, insertion of 2-norbornene into a Ru-H bond formed by sp^2 C-H bond activation of acrylate, and successive reductive elimination would give *cis*-**2**,[24,26,30e] whereas the predominant formation of *trans* isomers can not be explained. Time dependence of the codimerization of 2-norbornene with methyl acrylate under the reaction conditions shown in Scheme 1 was monitored by GLC, and the *trans*:*cis* ratio of **2a** was revealed to be approximately constant (>40:1) during the reaction, suggesting that no isomerization from the *cis* to the *trans* isomer occurs. Moreover, if the reaction proceeds

$$\text{norbornene} \quad + \quad \overset{\displaystyle}{\underset{\text{CO}_2{}^n\text{Bu}}{\diagup\!\!\!\diagdown}} \quad \xrightarrow[\textbf{solvent } 1.0 \text{ mL}, 130\,°\text{C}, 1\text{ h}]{\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{methyl acrylate})_2 \ (\textbf{4}) \ 0.050 \text{ mmol}} \quad \textit{exo-}\textbf{2d}$$

5.0 mmol   1.0 mmol

solvent:		
^{n}BuOH	79%	(3.8 : 1)
DMA	81%	(3.8 : 1)
diglyme	67%	(2.7 : 1)
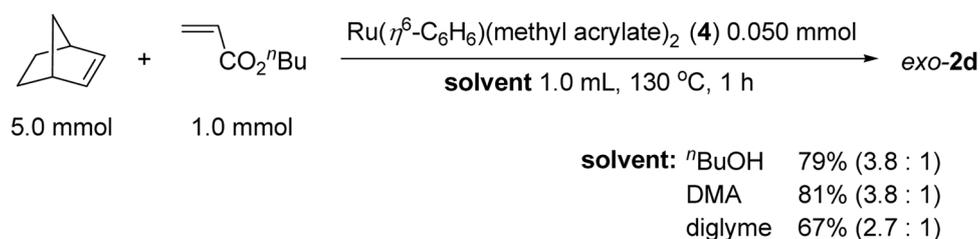
Figures in the parentheses are the ratio of *trans*- and *cis*-**2d**.

Scheme 2
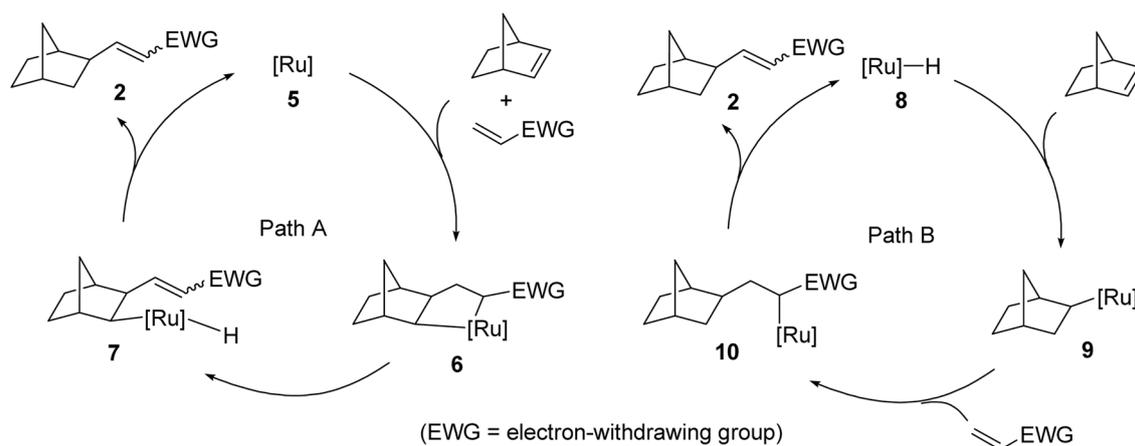
Scheme 3

via this pathway, acrylates having a substituent at the α-position or β-position should react with 2-norbornene; however, no reaction occurred, and therefore this pathway seems unlikely.

Synthesis of 2-Alkylidenetetrahydrofurans by Ruthenium-catalyzed Regio- and Stereoselective Codimerization of Dihydrofurans with α,β-Unsaturated Esters.[35] 2-Alkylidenetetrahydrofurans are versatile synthetic building blocks for natural products, such as macrotetrolide antibiotics,[36] and for artificial biologically active substances.[37] A large number of preparative methods for 2-alkylidenetetrahydrofurans have been reported so far, and are roughly classified into the following categories; acid or base-mediated cyclizations,[38,39] *cross*-Claisen condensation by nucleophilic reactions of ester enolates with lactones,[40] selenium[41]- or iodine[42]-involved cyclizations, and transition metal-catalyzed reactions.[43-45] Most of these methods, however, have an serious drawback inasmuch as undesirable byproducts, such as inorganic salts, are produced. On the other hand, codimerization of unsaturated hydrocarbons is an attractive carbon-carbon bond-forming method with high atom-efficiency. In the course of our investigation on ruthenium-catalyzed selective codimerization of alkenes,[29] we developed a highly regio- and stereoselective codimerization of dihydrofurans with α,β-unsaturated esters catalyzed by low-valent ruthenium complexes, which provides a novel and unique synthetic route to 2-alkylidenetetrahydrofurans.[46]

A reaction of 2,3-dihydrofuran (**11a**) with ethyl acrylate (**12a**) was first examined, and a zero-valent ruthenium complex, Ru(η^4-cod)(η^6-cot), was found to catalyze the codimerization efficiently in a polar solvent, *N,N*-dimethylacetamide (DMA), at 160 °C to give 2-(1-ethoxycarbonyl)ethylidene-

tetrahydrofuran (**13a**) in 70% yield, selectively (Scheme 4).

Catalytic activity of several low-valent ruthenium complexes for the codimerization of **11a** with **12a** was surveyed. Among other ruthenium complexes, Ru(η^6-cot)(η^2-dmfm)$_2$ [dmfm = dimethyl fumarate] was also effective to give **13a** in 70% yield. Ru(η^5-cyclooctadienyl)$_2$, Ru$_3$(CO)$_{12}$, and RuHCl(CO)(PPh$_3$)$_3$ showed moderate catalytic activity (**13a**, 50%, 45%, and 31% yield, respectively). CpRuCl(PPh$_3$)$_2$ [Cp = cyclopentadienyl], Cp*RuCl(η^4-cod) [Cp* = pentamethylcyclopentadienyl], RuH$_2$(PPh$_3$)$_4$, [RuCl$_2$(CO)$_3$]$_2$, and Ru(CO)$_3$(PPh$_3$)$_2$ were almost ineffective for the present codimerization. With other group 8-10 metal complexes, such as Fe$_3$(CO)$_{12}$, Co$_2$(CO)$_8$, RhCl(PPh$_3$)$_3$, IrCl(CO)(PPh$_3$)$_2$ and Pd(PPh$_3$)$_4$, no **13a** was obtained at all.

Effect of the reaction temperature on the codimerization of **11a** with **12a** was examined, and 160 °C was revealed to be suitable. The yield of **13a** decreased over 160 °C. The use of other solvents with high boiling point, such as diglyme, mesitylene, and *N,N*-dimethylformamide (DMF), resulted in a lower yield of **13a** (below 35% yield). Under the optimum reaction conditions, the scope of the codimerization of dihydrofurans with α,β-unsaturated esters was investigated (Table 2). The reaction of **12a** with 2-aryl-2,3-dihydrofurans proceeded nicely to give the corresponding codimers (entries 2 and 3). Remarkably, β-substituted unsaturated esters, such as methyl cinnamate (**12b**), methyl crotonate (**12c**), and dimethyl fumarate (**12d**), were also applicable to the present codimerization reaction (entries 5-7). Dimethyl maleate worked as well as **12d** to afford the identical codimer **13g** in 68% yield. The use of 2,5-dihydrofuran instead of **11a** in the codimerization with **12a** gave **13a** in 62% yield. In this case, isomerization of the substrate prior to the codimerization
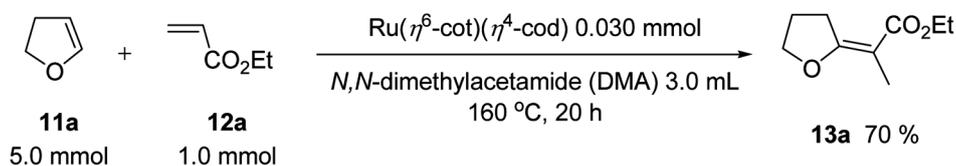
Scheme 4

Table 2. Ru(η^4-cod)(η^6-cot)-catalyzed codimerization of 2,3-dihydrofurans with α,β-unsaturated esters

entry	R^1	R^2	R^3	product		yield (%)[b]
1	H	H	Et	CO₂Et	**13a**	70 (59)
2	Ph	H	Et	CO₂Et	**13b**	39 (26)
3[b,c]	Np	H	Et	CO₂Et	**13c**	79 (65)
4	H	H	^{t}Bu	CO₂^{t}Bu	**13d**	72 (55)
5	H	Ph	Me	CO₂Me	**13e**	44 (19)
6	H	Me	Me	CO₂Me	**13f**	(11)
7	H	CO₂Me	Me	CO₂Me	**13g**	64 (55)

[a]GLC yield. Figures in the parentheses are isolated yield. [b]Np = 1-naphthyl. [c]48 h.

would occur. On the other hand, the codimerization of **11a** with α-substituted or β,β-disubstituted acrylates, 2(5*H*)-furanon, vinyl ketones, acrylonitrile and acrylamides did not proceed under the present reaction conditions. In addition, six-membered unsaturated cyclic ethers, such as 3,4-dihydro-2*H*-pyran, 1,4-dioxene, and *n*-butyl vinyl ether did not give the corresponding codimers in the reaction with **12a**.

A deuterium-labeling experiment was conducted to elucidate the reaction mechanism with deuterium-incorporated dimethyl fumarate (**12d**-d_2). The codimer **13g**-d_2 was iso-

lated in 50% yield with 29% and 36% deuterium incorporations as shown in Scheme 5. The decrease of the deuterium contents in **13g**-d_2 implies that a rapid H/D exchange occurred during the reaction, that is promoted by an in situ-generated ruthenium hydride species. We believe that the hydride should be supplied from a cod ligand in Ru(η^4-cod)(η^6-cot) or an olefinic hydrogen of α,β-unsaturated esters *via* an sp^2 C-H bond activation.

A proposed mechanism is illustrated in Scheme 6. An (alkyl)ruthenium complex **15** would be formed by the insertion of α,β-unsaturated ester **12** into the Ru-H bond of the catalytically active ruthenium hydride species **14**. At this stage, an electron-withdrawing alkoxycarbonyl group should be placed at the α-position. Successive insertion of **11** into the Ru-C bond in **15** gives a (tetrahydrofuranyl)ruthenium species **16**, where an electronic factor seems to be predominant to control the insertion direction. β-Hydrogen elimination of intermediate **16** gives **17**. Addition of a ruthenium hydride species and β-hydrogen elimination occur twice to give a 2-alkylidenetetrahydrofuran (**13**) with regeneration of a ruthenium hydride species **14**.

The decrease of deuterium incorporation in Scheme 5 can be explained by a mechanism involving **20**-d_1 which would be produced by addition of an in situ generated [Ru]-D to 2,5-dihydrofuran.

It is noted that (*E*)-**13h** is thermally more stable than (*Z*)-**13h** by 5 kcal/mol, calculated by a DFT method at the B3LYP/6-31G** level (Chart 1).

A metallacycle mechanism can be considered as an alternative pathway; in this case, however, linear codimers should be obtained rather than the branched ones, **13a-13d**, because the alkoxycarbonyl group would prefer to occupy the α-position in the metallacycle intermediate. Moreover, the decrease of deuterium incorporation in Scheme 5 can not be explained by this mechanism.

Regio- and Stereoselective Synthesis of Enamides by Ruthenium-catalyzed Co-oligomerization of *N*-Vinyl-amides with Alkenes.[47] Enamides are contained in many natural products such as salicylihalamide[48] and lobatamide,[49] and have recently been synthesized using transition metal catalysts, as represented by (a) the vinylation of amides,[50] (b) the chelation-assisted coupling reaction of *N*-vinylamides with 1,3-butadiene,[51] (c) the addition of amides to alkynes,[52] (c) the oxidative amidation of alkenes,[53] and (d) the isomerization of *N*-allylamides.[54]

In considering potential new methods for the synthesis of

Scheme 5

Scheme 6

(E)-13h
0.0 kcal/mol

(Z)-13h
+ 5.0 kcal/mol
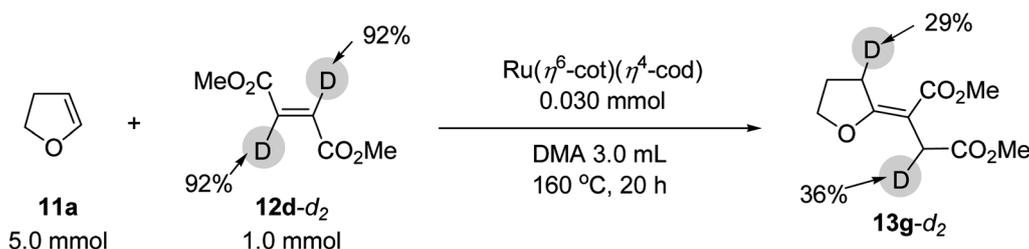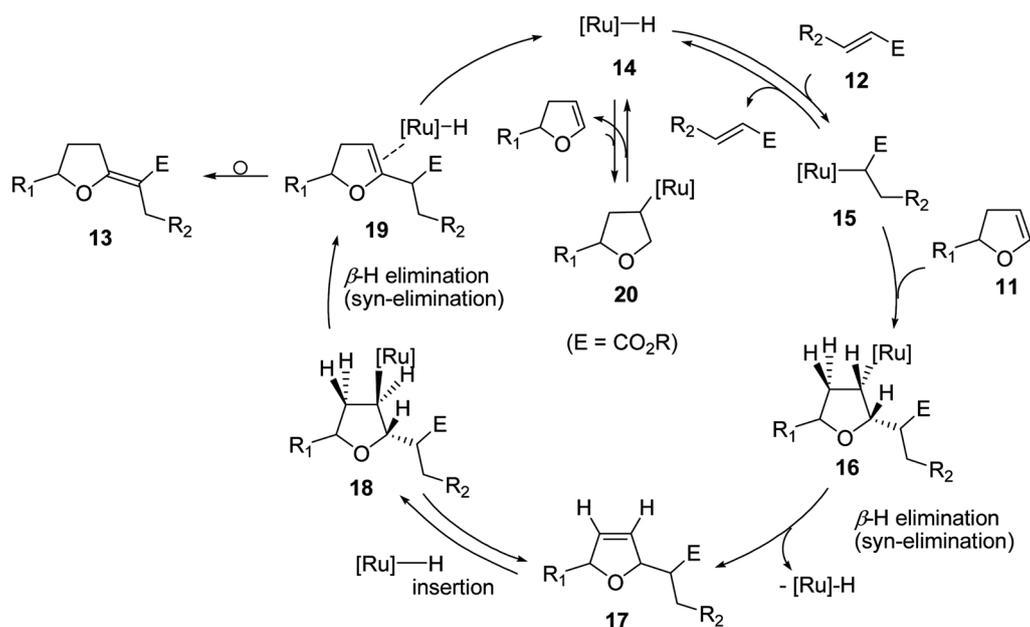
Chart 1

enamides, we have focused our efforts on ruthenium-catalyzed regio- and stereoselective co-oligomerization reactions. Many examples of transition metal complex-catalyzed codimerization reactions of *alkenes with alkynes* have been reported.[4] In sharp contrast, codimerization as well as co-oligomerization reactions of *"different alkenes"* are still quite difficult except for hydrovinylation of styrenes,[9-14] and a challenging subject in modern organic and organometallic chemistry.[29,35] We report here zero-valent ruthenium complex-catalyzed codimerization reaction of *different alkenes*; *i.e.*, a codimerization reaction of *N*-vinylamides with alkenes as well as a co-oligomerization reaction of *N*-vinylamides, acrylates, and ethylene, which offer novel and atom-economical methods for synthesis of enamides with high regio- and stereoselectivity in one step.[55]

Treatment of *N*-methyl-*N*-vinylacetamide (**21a**, 1.1 mmol) with ethyl acrylate (**22a**, 1.0 mmol) in the presence of a catalytic amount of Ru(η^6-cot)(η^2-dmfm)$_2$ (0.020 mmol) in

N,N-dimethylacetamide (DMA)[35,56] (3.0 mL) at 160 °C for 3 h gave the linear codimer, ethyl 5-(*N*-methylacetylamino)-pent-4-enoate (**23a**), in 90% yield with 95% *E* selectivity (Scheme 7).

First, the catalytic activity of several low-valent ruthenium complexes for the codimerization of **21a** with **22a** was examined. Besides Ru(η^6-cot)(η^2-dmfm)$_2$, Ru(η^5-cyclooctadienyl)$_2$ (**23a**, 81%) and Ru(η^4-cod)(η^6-cot) (**23a**, 78%) showed high catalytic activity, while other zero-valent ruthenium complexes, such as Ru$_3$(CO)$_{12}$ (**23a**, 6%) and Ru(CO)$_3$(PPh$_3$)$_2$ were ineffective. No catalytic activity of divalent ruthenium complexes, such as Cp*RuCl(η^4-cod), [RuCl$_2$(CO)$_3$]$_2$, RuH$_2$(PPh$_3$)$_4$, and RuHCl(CO)(PPh$_3$)$_3$, was observed in the present reaction.

The present reaction required a temperature of over 150 °C for complete conversion of both substrates, and the best result was obtained at 160 °C (**23a**, 90%). However, at 170 °C, the reaction became sluggish, and the yield of **23a** decreased to 65%.

Several enamides were prepared by this method in good to high yields with high *E* selectivity (Scheme 8). Electron-deficient alkenes are suitable for the present reaction; for example, codimerization of *N*-methyl-*N*-vinylacetamide (**21a**) with ethyl vinyl ketone (**22c**) or dimethyl maleate (**22d**) gave **23c** and **23d** in respective yields of 70% and 76%. Although 2-norbornene (**22e**) and ethylene (**22f**) could also

21a
1.1 mmol

22a
1.0 mmol

Ru(η^6-cot)(η^2-dmfm)$_2$ 0.020 mmol
DMA 3.0 mL, 160 °C, 3 h

23a
90% (72% isolated yield)
(95% *E* form)

Scheme 7

21
1.1 mmol

22
1.0 mmol

23

(5)

21a : $R^1 = R^2 = Me$ **22b** : $R^3 = H$, $R^4 = CO_2{}^tBu$ **23b** : 77 (61)% (88% *E* form)
21a : $R^1 = R^2 = Me$ **22c** : $R^3 = H$, $R^4 = COEt$ **23c** : 70 (48)% (94% *E* form)
21a : $R^1 = R^2 = Me$ **22d** : $R^3 = R^4 = CO_2Me$ **23d** : 76 (52)% (98% *E* form)

21a : $R^1 = R^2 = Me$ **22e** : $R^3 = R^4 = $ **23e** : 33%   (99% *E* form, and *exo* only)[a]

21a : $R^1 = R^2 = Me$ **22f** : $R^3 = R^4 = H$ **23f** : 16%   (97% *E* form)[b]
21b : R^1, $R^2 = -(CH_2)_5-$ **22a** : $R^3 = H$, $R^4 = CO_2Et$ **23g** : 60 (50)% (88% *E* form)

Scheme 8. Yield was determined by GLC. Figures in the parentheses are isolated yield. [a]2-Norbornene (5.0 mmol). [b]Ethylene (10 atm).

21
1.1 mmol

22
excess

24

Isolated yield

21a: $R^1 = R^2 = Me$ **22a** : $R^4 = CO_2Et$ **24a** : 54%[a]
21a: $R^1 = R^2 = Me$ **22f** : $R^4 = H$ **24b** : 63%[b]
21b: R^1, $R^2 = -(CH_2)_5-$ **22a** : $R^4 = CO_2Et$ **24c** : 48%[a]
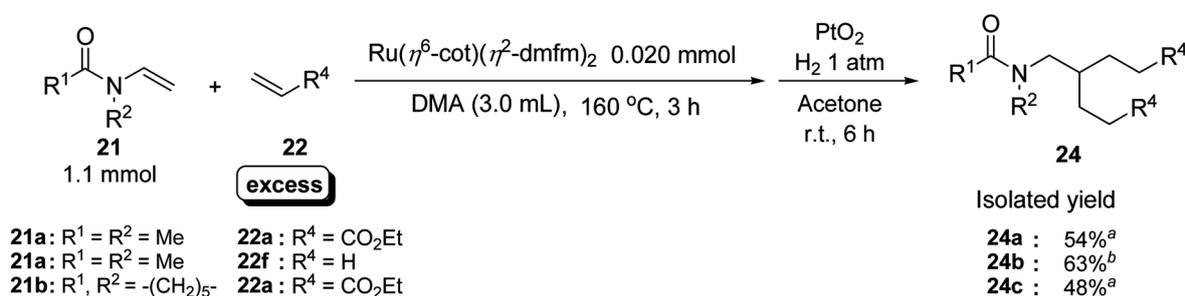
Scheme 9. [a]Ethyl acrylate (10 mmol). [b]Ethylene (40 atm).

be used, the yields of the codimers, **23e** (*exo* only) and **23f**, were rather low. For synthesis of **23f**, higher ethylene pressure promoted 1:2 co-oligomerization of **21a** with **22f** (*vide infra*). *N*-Vinylcaprolactam (**21b**) also reacted with ethyl acrylate (**22a**) to give the desired enamide, ethyl 5-(2-oxo-azaperhydroepinyl)pent-4-enoate (**23g**), in 60% yield.

In the present reaction, only *N*-vinylamides worked well and no codimerization occurred between other vinylamide derivatives, such as 3-vinyl-2-oxazolidinone (**21c**) or *N*-methyl-*N*-vinyl-*p*-toluenesulfonamide (**21d**), and ethyl acrylate (**22a**) even under the optimum reaction conditions. A chelating effect of *N*-vinylamides toward an active ruthenium species should play an important role in the catalytic cycle (*vide infra*). On the other hand, treatment of *N*-vinylamides (**21**) with a large excess amount of alkenes (**22**) under the same catalytic reaction conditions followed by hydrogenation gave 1:2 co-oligomers (**24**) in up to 63% yield (Scheme 9).

This means that double C-C bond-formation proceeded selectively at the *β*-position of a vinyl group in *N*-vinyl-amides (**21**). In addition, codimerization reaction of the isolated enamide **23a** with **22a** proceeded by the present catalyst system to give **24a** in an isolated yield of 56% after hydrogenation. This result strongly suggests that the present co-oligomerization proceeds stepwise and substituted *N*-vinylamides would be generally applicable to the present reaction.

Then, we attempted to develop a three-component coupling reaction of different alkenes. After many trials, we realized this reaction through the combination of *N*-vinylamides (**21**), ethyl acrylate (**22a**) and ethylene (**22f**) (40 atm). Hydrogenation of the generated isomeric cotrimers gave **25** as a single product in up to 66% yield (Scheme 10). To the best of our knowledge, the selective cotrimerization reaction of two or three different alkenes had never been accomplished before.

21
1.1 mmol

22a
1.0 mmol

Isolated yield

25a: 66%
25b: 58%

21a: $R^1 = R^2 = Me$
21b: R^1, $R^2 = -(CH_2)_5-$
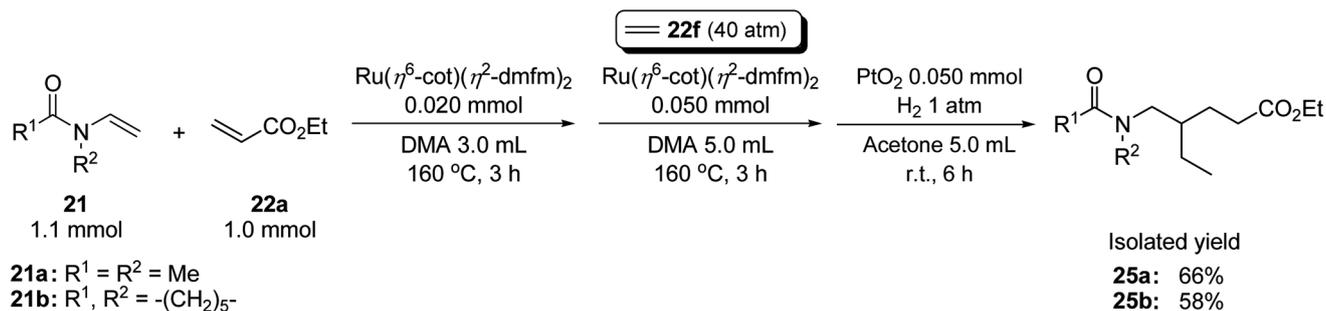
Scheme 10
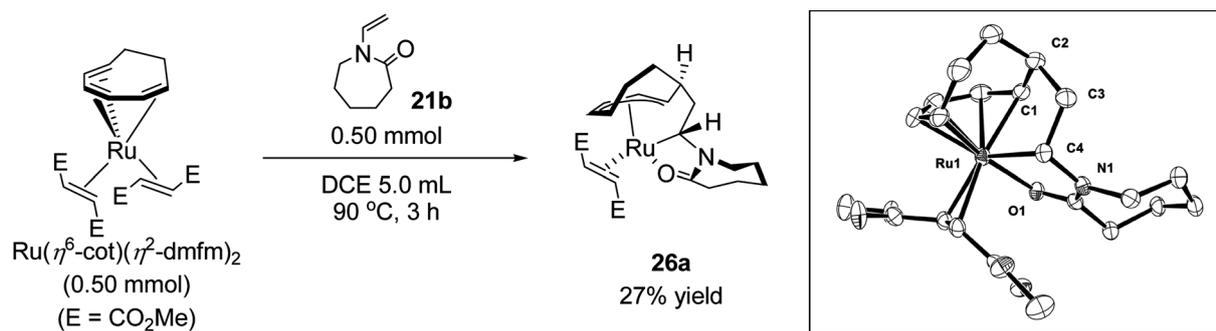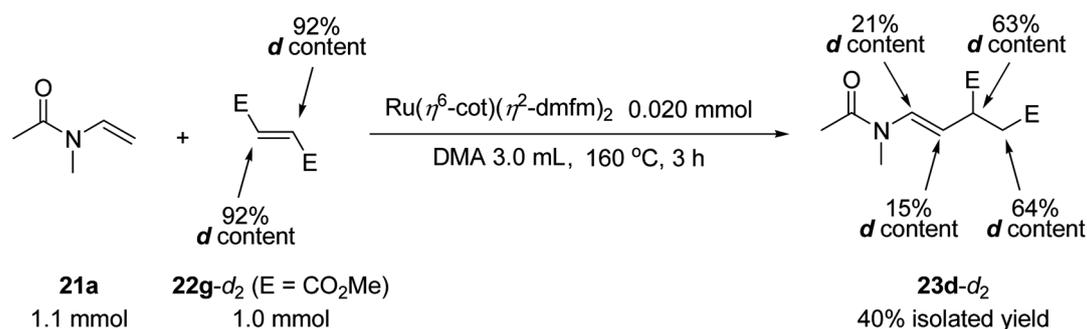
Scheme 11

Scheme 12

To investigate the mechanism, the reaction of **21a** with dimethyl fumarate-d_2 (**22g**-d_2) was carried out in the presence of Ru(η^6-cot)(η^2-dmfm)$_2$ catalyst in DMA at 160 °C for 3 h to give the deuterium-scrambled enamide (**23d**-d_2) in an isolated yield of 40% (Scheme 11). This deuterium-scrambling could be explained by the formation of a ruthenium hydride species at an early stage in the catalytic cycle (*vide infra*).

A stoichiometric reaction of Ru(η^6-cot)(η^2-dmfm)$_2$ with *N*-vinylcaprolactam (**21b**) in 1,2-dichloroethane (DCE) at 90 °C for 3 h under an argon atmosphere gave a new complex **26a** (27% isolated yield, Scheme 12).[57] This complex could be obtained by a ligand-exchange reaction of one molecule of dmfm with *N*-vinylcaprolactam, followed by oxidative cyclization between a cot ligand and a vinyl group of *N*-vinylcaprolactam. Complex **26a** also showed good catalytic activity for the codimerization of **21b** with **22a** to give **23g** in 56% yield.

Considering all of the results described above, we postulated the following mechanism for the present codimerization of *N*-vinylamides (**21**) with alkenes (**22**) (Scheme 13). The reaction starts with the removal of a cot ligand in Ru(η^6-cot)(η^2-dmfm)$_2$ by *N*-vinylamides (**21**) *via* metallacycle formation of **26** and reductive elimination[58] to give coordinatively unsaturated zero-valent ruthenium species, which is effective for the formation of a ruthenium hydride species *via* activation of sp^2 C-H bonds in alkenes or a dmfm ligand.[59] Alkenes (**22**) are then inserted into a Ru-H bond, followed by the successive chelation-assisted insertion of *N*-vinylamides into a Ru-C bond (*vide supra*). Subsequent β-hydrogen elimination gives the products **23**, with regenera-

tion of an active ruthenium hydride species. At this stage, a mechanism that involves oxidative cyclization of *N*-vinyl-amides with alkenes to give a ruthenacyclopentane intermediate could not be completely excluded, however, the result of deuterium-scrambling shown in Scheme 11 can be reasonably explained by a mechanism that involves the formation of a ruthenium hydride species.

Highly Selective Ruthenium Complex-catalyzed Dimerization of Styrenes and Linear Codimerization of Styrenes with Ethylene.[60] The first transition metal complexes that were shown to catalyze the homo-dimerization of styrenes were based on palladium.[61] Later, nickel[62]- and zirconium[63]-based catalyst systems were shown to be effective for this dimerization reaction, and these generally gave a head-to-tail dimer, (*E*)-1,3-diaryl-1-butenes. There has been only one previous example of head-to-head dimerization to give (*E*)-1,4-diaryl-1-butene; by Kretschmer *et al.*[18] using a bis(indenyl)yttrium hydride as a catalyst. However, their catalyst system is unwieldy because of the instability of the catalyst toward air and moisture.

On the other hand, the transition metal complex-catalyzed codimerization of styrenes with ethylene generally gave the head-to-tail dimers, 3-aryl-1-butenes, and an enantioselective version has recently been developed.[13,14]

In the course of our study on the synthesis and catalytic activity of low-valent ruthenium complexes[28c,e] as well as ruthenium-catalyzed codimerization reactions of different alkenes,[29,35,47] we found that a zero-valent ruthenium complex, Ru(η^6-cot)(η^2-dmfm)$_2$, in the presence of primary alcohols efficiently catalyzes an unusual *head-to-head* dimerization of styrenes to give (*E*)-1,4-diaryl-1-butenes.[64,65]

Scheme 13

Scheme 14

RuHCl(CO)(PPh$_3$)$_3$, RuCl$_2$(PPh$_3$)$_3$, and Cp*RuCl(η^4-cod).

The effect of the solvent in the presence of 1-propanol was then examined. In the present reaction, mesitylene was the best solvent, and **28a** was obtained in 67% yield. The reaction also proceeded in toluene (**28a**, 51%), 1,4-dioxane (**28a**, 50%), and diglyme (**28a**, 33%), while **28a** was not obtained in *N*,*N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) due to their strong ability to coordinate to an active ruthenium species. The concomitant use of primary alcohols is essential for the success of the present reaction (*vide infra*); however, when 1-propanol was used as a solvent (without mesitylene), the yield of **28a** decreased to 57%.

The kind and the amount of alcohols are critical for the success of the present catalytic reaction. No reaction occurred without primary alcohols, such as ethanol, 1-propanol, and 1-octanol. Secondary and tertiary alcohols were not suitable for this reaction. As for low-boiling-point primary alcohols, such as ethanol and 1-propanol, 3 equivalents (6.0 mmol) with regard to styrene (**27a**) were required (**28a**, 64% for ethanol and **28a**, 67% for 1-propanol). In sharp contrast, when 3 equivalents of 1-octanol were used, the reaction became sluggish, and undesirable byproducts, such as 1-octanal and octyl octanoate, as well as a considerable amount of ethylbenzene derived from hydrogenation of styrene (**27a**), were produced (**28a**, 19%). To suppress the formation of these byproducts, the amount of 1-octanol was reduced from 6.0 mmol to 0.50 mmol and the reaction was carried out at lower reaction temperature at 80 °C to give **28a** in the best yield of 80% with high (*E*)-selectivity (95%).

Under the optimum reaction conditions, the corresponding head-to-head dimers (**28a-d**) were obtained from styrenes (**27a-d**) in good to high yields with high regio- and stereo-selectivity (Scheme 15). As described above, 1-octanol was most effective for styrenes (**27a**, **27b**, and **27d**), while 1-propanol was suitable for **27c** at 110 °C. When the reaction of **27c** was carried out in the presence of 1-octanol instead of 1-propanol at 80 °C, the yield of **28c** decreased from 66% to 40%. No significant effect was observed for the substituents on the phenyl ring in styrenes.

The time-course of the dimerization of **27a** to **28a** was shown in Figure 1, which clearly indicated the presence of an induction period. This suggests that a real catalytically active species would be formed from Ru(η^6-cot)(η^2-dmfm)$_2$ and 1-octanol at the early stage of the reaction. The yield of **28a** markedly increased about 5 h after the reaction started (TOF 2.0 h^{-1}, 5 to 8 h), and total TON was 16.2 after 50 h.

This catalyst system is also effective for the selective linear codimerization of styrenes with ethylene, to give (*E*)-1-aryl-1-butenes in good yields with high selectivity.

First, the catalytic activity of several ruthenium complexes was examined in the dimerization of styrene (**27a**) to a head-to-head dimer (**28a**) (Scheme 14).

Among the complexes examined, Ru(η^6-cot)(η^2-dmfm)$_2$ showed the highest catalytic activity, and **28a** was obtained in 67% yield with high (*E*)-selectivity (95%). Ru(η^4-cod)-(η^6-cot) and Ru(η^5-C$_8$H$_{11}$)(η^5-C$_6$H$_5$O)·PhOH[66] also showed moderate catalytic activity to give **28a** in respective yields of 36% and 25% ((*E*)-isomer, 95%), while no reaction occurred with divalent ruthenium complexes, such as [RuCl$_2$(CO)$_3$]$_2$, [RuCl$_2$(η^4-cod)]$_n$, [RuCl$_2$(η^6-*p*-cymene)]$_2$, RuH$_2$(PPh$_3$)$_4$,

Scheme 15. [a]Figures in the parentheses are isolated yield. [b]1-PrOH (6.0 mmol) at 110 °C.
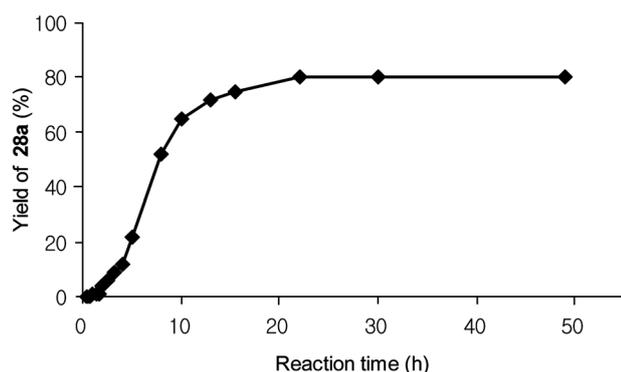
Figure 1. The time-course of dimerization of **27a** to **28a**.

To elucidate the mechanism of this reaction, a deuterium-labeling experiment using ethanol-d_1 was performed in the dimerization of styrene (**27a**) to **28a**. The reaction gave a mixture of mono-deuterio (*E*)-1,4-diphenyl-1-butenes (**28a-d_1**, M^+ = 209), predominantly, and almost no **28a-d_2** (M^+ = 210) or **28a-d_3** (M^+ = 211) was obtained. Based on the results of an NMR study, a deuterium was distributed at four positions in **28a-d_1** (Scheme 16).

This deuterium-scrambling suggests the formation of a ruthenium hydride ([Ru]-H) as well as ruthenium-deuteride ([Ru]-D), which promote the rapid H/D exchange of the starting styrene (**27a**) to **27a-d_1** *via* an addition/β-hydrogen elimination mechanism. When isolated **28a** and **28a-d_1** were respectively treated with ethanol-d_1 under the same reaction conditions, neither deuterium incorporation for **28a** nor a change in the deuterium distribution of **28a-d_1** was observed. This result strongly suggests that deuterium exchange occurred with the starting styrene (**27a**), and not with the formed **28a**. This can also explain why the present reaction gave only dimers, and not trimers or oligomers.

Although the reaction mechanism is not yet clear, three possible mechanisms are illustrated in Scheme 17. In Path A, the oxidative addition of an sp² C-H bond in styrene (**27**) to a Ru(0) species proceeds to give a (hydrido)(alkenyl)-ruthenium intermediate. Subsequent insertion of **27** into either a [Ru]-H bond or an alkenyl-[Ru] bond, followed by reductive elimination would give dimer **28**. In Path B, a [Ru]-H species is first generated by the oxidative addition of primary alcohols to a Ru(0) species. Successive double insertion of **27** and stereoselective β-hydrogen elimination give the corresponding dimer **28** with regeneration of a [Ru]-H species. Path C involves the oxidative cyclization of two molecules of **27** on a Ru(0) species to give a ruthena-cyclopentane intermediate.[67] The ring-opening of a ruthena-
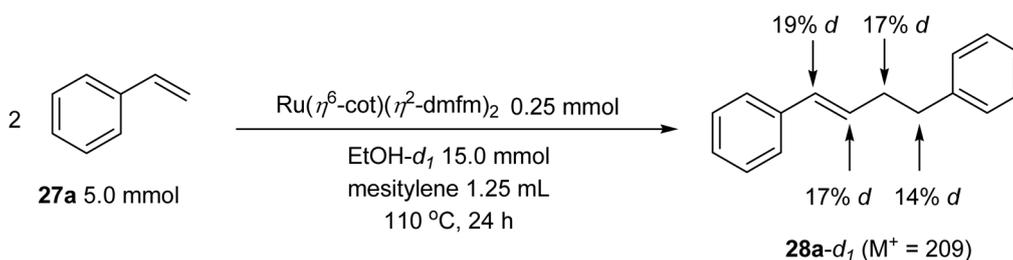
Scheme 16
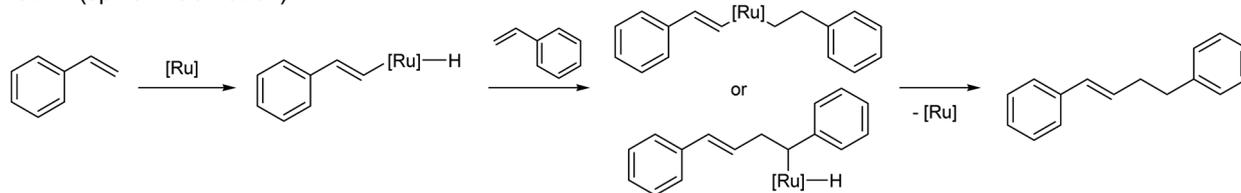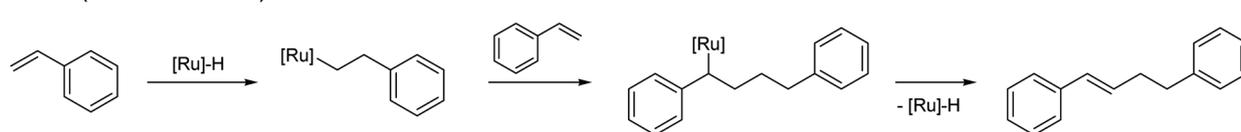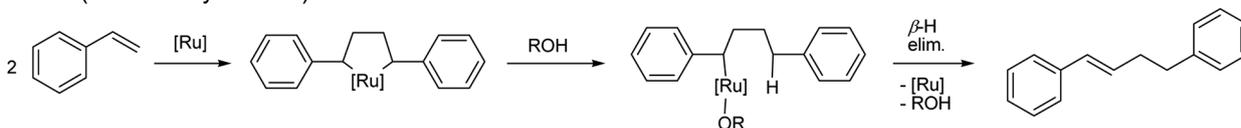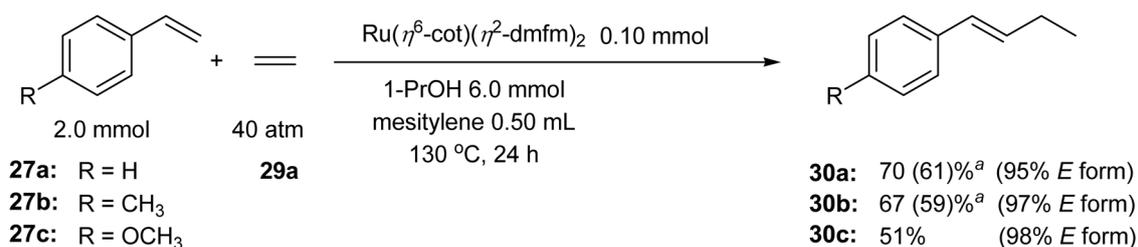
Scheme 17

Scheme 18. *a*Figures in deparantheses are isolated yield.

cyclopentane by the primary alcohol, followed by stereo-selective β-hydrogen elimination would give dimer **28**. If Path B is operative, an initial 1,2-insertion of styrene (**27**) into a [Ru]-H bond should be considered despite the well-known electronic preference of styrenes for 2,1-insertion,[68] even in the case of ruthenium. Therefore, we suggest that the present reaction might occur according to Path C. The ring-opening of a ruthenacyclopentane by the direct β-hydrogen elimination is not a favored process, but this could be facilitated by protonation or σ-bond metathesis[69] with the primary alcohol, which plays the role of co-catalyst. Then, the stereoselective β-hydrogen elimination could occur to give dimer **28** with regeneration of the Ru(0) species and the primary alcohol co-catalyst.

In addition, the present catalyst system is effective for the regio- and stereoselective linear codimerization of styrenes (**27a-c**) with ethylene (**29a**). As described previously, transition metal complex-catalyzed codimerization of styrenes with ethylene generally gave 3-aryl-1-butenes (hydrovinyl-ation), while unusual codimers, (*E*)-1-aryl-1-butenes (**30a-c**), were obtained by the present catalyst system in good yields and with high selectivity (Scheme 18).

Conclusion

This account is a summary of our studies on ruthenium-catalyzed highly selective codimerization and co-oligomerizations of two or three different alkenes. Low-valent ruthenium complexes represented by Ru(η^6-cot)(η^2-dmfm)$_2$ showed high catalytic activity for a variety of regio-, stereo-, and chemoselective codimerization and co-oligomerization of alkenes. The reactions developed in this study are all atom-economical and environmentally benign processes. We hope these findings will offer new methods for the synthesis of novel functional monomers from versatile and inexpensive starting materials.

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3619 measured reflections were collected on a Rigaku Saturn CCD diffractometer at 143 K (2$θ$ < 55.0°). R_1 = 0.0376, wR_2 = 0.0356. CCDC-640650 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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