Homogeneous Catalysis

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Highly Selective Dimerization of Styrenes and Linear Co-dimerization of Styrenes with Ethylene Catalyzed by a Ruthenium Complex**

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In memory of Yoshihiko Ito

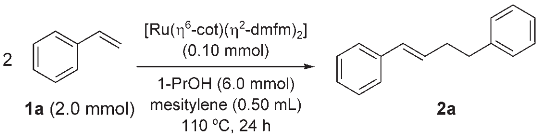
The homo- and co-dimerization of alkenes are important methods for generating higher alkenes, which are a source of new kinds of polymers, lubricants, detergents, and many other useful chemicals.[1] Considerable attention has recently been focused on these reactions, because of the demand for atom-efficient organic syntheses, that is, all of the atoms in the starting materials are incorporated into the products (100 % atom economy).[2]

The first transition-metal complexes that were shown to catalyze the homo-dimerization of styrenes were based on palladium.[3] Later, nickel-[4] and zirconium-based[5] catalyst systems were shown to be effective for this dimerization reaction, and these generally gave head-to-tail dimers, namely (*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: Kretschmer et al.[6] reported that the use of a bis(indenyl)yttrium hydride as the catalyst gave such a dimerization. However, their catalyst is unstable towards air and moisture.

The co-dimerization of styrenes with ethylene has also been extensively studied since it was first reported in 1965.[7] Many transition-metal complexes are active in this process,[8,9] and catalysts containing nickel are the most active.[10,11] The products are head-to-tail dimers (3-aryl-1-butenes), and an enantioselective version of the co-dimerization (hydrovinylation) of styrenes with ethylene has recently been developed.[11,12]

In the course of our study on the synthesis and catalytic activity of low-valent ruthenium complexes[13] as well as ruthenium-catalyzed co-dimerization reactions of different alkenes,[14] we found that the zero-valent ruthenium complex $[Ru(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2]$[15] (cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate) in the presence of primary alcohols efficiently catalyzes an unusual head-to-head dimerization of styrenes to give (*E*)-1,4-diaryl-1-butenes.[16,17] This catalyst system is also effective for the selective linear co-dimerization of styrenes with ethylene to give (*E*)-1-aryl-1-butenes in good yields and high selectivity.

The catalytic activity of several ruthenium complexes was initially examined in the dimerization of styrene (**1a**) to give the head-to-head dimer **2a** [Eq. (1)].



(1)

Of the complexes examined, $[Ru(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2]$ showed the highest catalytic activity, and **2a** was obtained in 67 % yield with high *E* selectivity (95 %). $[Ru(\eta^4\text{-cod})(\eta^6\text{-cot})]$ (cod = 1,5-cyclooctadiene) and $[Ru(\eta^5\text{-}C_8H_{11})(\eta^5\text{-}C_6H_5O)]\cdot PhOH$[18] also showed moderate catalytic activity to give **2a** in respective yields of 36 % and 25 % (*E* isomer, 95 %), while no reaction occurred with divalent ruthenium complexes, such as $[\{RuCl_2(CO)_3\}_2]$, $[RuCl_2(\eta^4\text{-cod})]_n$, $[\{RuCl_2(p\text{-cymene})\}_2]$, $[RuH_2(PPh_3)_4]$, $[RuHCl(CO)(PPh_3)_3]$, $\{RuCl_2(PPh_3)_3)]$, and $[Cp^*RuCl(\eta^4\text{-cod})]$ (Cp* = pentamethylcyclopentadienyl).

The effect of the solvent in the presence of 1-propanol was then examined. In the present reaction, mesitylene proved to be the best solvent, and **2a** was obtained in 67 % yield. The reaction also proceeded in toluene (**2a**, 51 %), 1,4-dioxane (**2a**, 50 %), and diglyme (**2a**, 33 %). In contrast, **2a** was not obtained in *N*,*N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) because of 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 (see below); however, when 1-propanol was used as the solvent without mesitylene, the yield of **2a** decreased to 57 %.

The type and the amount of alcohols used are critical for the success of the present catalytic reaction. No reaction occurred without the presence of primary alcohols, such as ethanol, 1-propanol, and 1-octanol. Secondary and tertiary alcohols were not suitable for this reaction. Three equivalents (6.0 mmol), relative to styrene (**1a**)), of low-boiling-point

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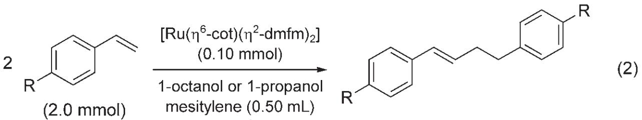
primary alcohols, such as ethanol and 1-propanol, were required to give **2a** (64% for ethanol and 67% for 1-propanol). In sharp contrast, when three equivalents of 1-octanol were used, the reaction became sluggish, and undesirable by-products, such as 1-octanal and octyl octanoate, as well as a considerable amount of ethylbenzene derived from the hydrogenation of styrene (**1a**), were produced (**2a**, 19%). To suppress the formation of these by-products, the amount of 1-octanol was reduced from 6.0 mmol to 0.50 mmol and the reaction was carried out at a lower reaction temperature (80°C) to give **2a** in the highest yield of 80% with high *E* selectivity (95%).

Under the optimum reaction conditions, the corresponding head-to-head dimers (**2a–d**) were obtained from styrene derivatives **1a–d** in good to high yields with high regio- and stereoselectivity [Eq. (2); figures in the parentheses give yield of isolated product]. As described above, 1-octanol (0.50 mmol) was most effective for styrene derivatives **1a**, **1b**, and **1d**, while 1-propanol (6.0 mmol) was suitable for **1c** when the reaction was performed at 110°C. When the reaction of **1c** was carried out in the presence of 1-octanol instead of 1-propanol at 80°C, the yield of **2c** decreased from 66% to 40%. No significant effect was observed for substituents on the phenyl ring of the styrene derivatives.



(2)

1a: R = H
1b: R = CH_3
1c: R = OCH_3
1d: R = F

2a: 80 (53)% (95% *E* form)
2b: 71% (95% *E* form)
2c: (66)% (97% *E* form)
2d: 67 (56)% (97% *E* form)

The time-course of the dimerization of **1a** to **2a** is shown in Figure 1, which clearly indicates the presence of an induction period. This finding suggests that a catalytically active species is formed from $[Ru(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2]$ and 1-octanol in the initial stages of the reaction. The yield of **2a** markedly increased about 5 h after the start of the reaction (turnover frequency (TOF) = 2.0 h^{-1}, 5–8 h), and total turnover number (TON) was 16.2 after 50 h.

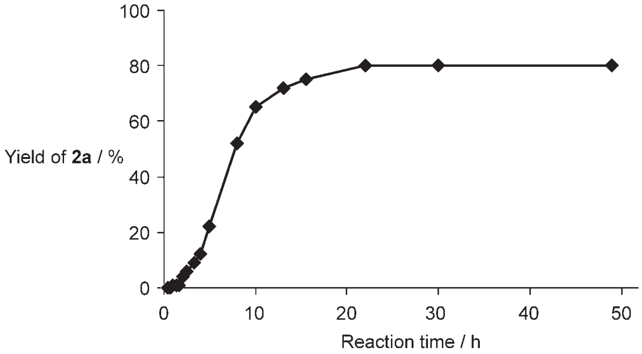
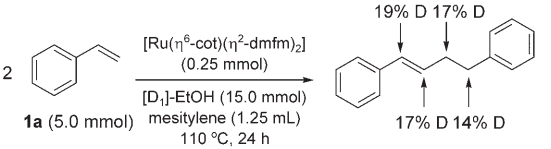


Figure 1. The time-course of the dimerization of **1a** to **2a**.

To elucidate the mechanism of this reaction a deuterium-labeling experiment using $[D_1]$ethanol was performed for the dimerization of styrene (**1a**) to give **2a**. The reaction gave a mixture of mono-deuterio-(*E*)-1,4-diphenyl-1-butenes ($[D_1]$-**2a**, $m/z = 209$ $[M^+]$), predominantly, and almost no $[D_2]$-**2a** ($m/z = 210$ $[M^+]$) or $[D_3]$-**2a** ($m/z = 211$ $[M^+]$) was obtained. An NMR study showed that a deuterium atom was distributed at four positions in $[D_1]$-**2a** [Eq. (3)].



1a (5.0 mmol)

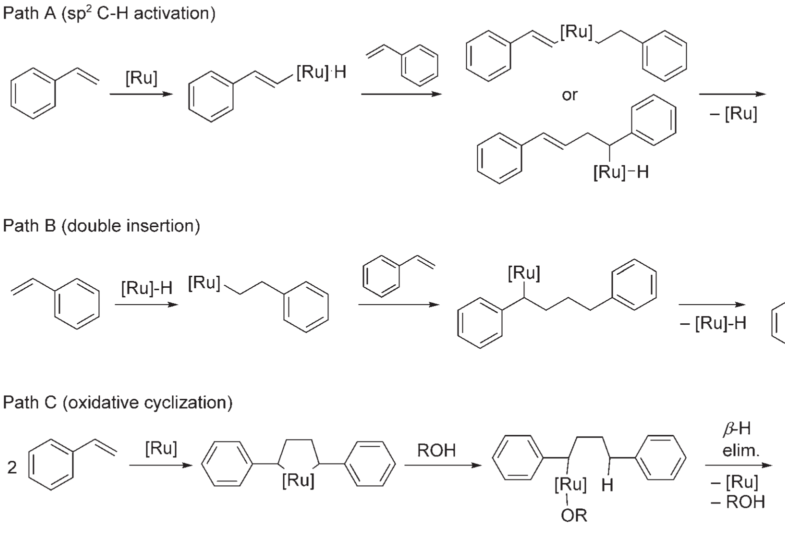
$[D_1]$-**2a** ($M^+ = 209$)

(3)

This deuterium scrambling suggests the formation of a ruthenium hydride ([Ru]-H) species as well as a ruthenium deuteride ([Ru]-D) species, which promote the rapid H/D exchange of the starting styrene (**1a**) to $[D_1]$-**1a** through an addition/β-hydrogen elimination mechanism. When isolated **2a** and $[D_1]$-**2a** were respectively treated with $[D_1]$ethanol under the same reaction conditions, neither deuterium incorporation into **2a** nor a change in the deuterium distribution of $[D_1]$-**2a** was observed. This result strongly suggests that deuterium exchange occurs with the starting styrene (**1a**), and not with the formed **2a**. This proposal can also explain why the present reaction gave only dimers and not trimers or oligomers.

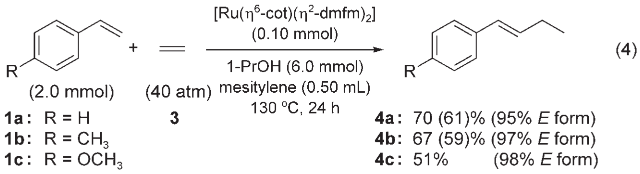
Although the reaction mechanism is not yet clear, three possible mechanisms are illustrated in Scheme 1. In path A, the oxidative addition of an sp^2 C–H bond in styrene (**1a**) to a Ru^0 species proceeds to give a (hydrido)(alkenyl)ruthenium intermediate. Subsequent insertion of **1a** into either a [Ru]–H bond or an alkenyl–[Ru] bond, followed by reductive elimination would give dimer **2a**. 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 **1a** and stereoselective β-hydrogen elimination give the corresponding dimer **2a** with regeneration of a [Ru]-H species. Path C involves the oxidative cyclization of two molecules of **1a** onto a Ru^0 species to give a ruthenacyclopentane intermediate.[19] The ring-opening of a ruthenacyclopentane by the primary alcohol, followed by a stereoselective β-hydrogen elimination would give dimer **2a**. If path B is operative, an initial 1,2-insertion of styrene (**1a**) into a [Ru]–H bond should be considered despite the well-known electronic preference of styrenes for 2,1-insertion,[20] even in the case of a ruthenium species. 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[21] with the primary alcohol, which plays the role of co-catalyst. Then, the stereoselective β-hydrogen elimination could occur to give dimer **2a** with regeneration of the Ru^0 species and the primary alcohol co-catalyst.

The present catalyst system is also effective for the regio- and stereoselective linear co-dimerization of styrenes (**1a–c**)



Scheme 1. Possible reaction pathways. [Ru] = ruthenium complex.

with ethylene (**3**). As described previously, co-dimerization of styrenes with ethylene catalyzed by a transition-metal complex generally gave 3-aryl-1-butenes (hydrovinylation), while unusual co-dimers, namely (*E*)-1-aryl-1-butenes (**4a**–**c**), were obtained in good yields and with high selectivity with the present catalyst system [Eq. (4); figures in the parentheses give yield of isolated product].



In conclusion, we have developed a novel catalyst system consisting of $[Ru(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2]$ in the presence of primary alcohols to produce unusual head-to-head dimers of styrenes, namely (*E*)-1,4-diaryl-1-butenes, as well as linear co-dimers of styrenes with ethylene, namely (*E*)-1-aryl-1-butenes, in good yields with high regio- and stereoselectivity.

Experimental Section

General procedures: All manipulations were performed in an argon atmosphere by standard Schlenk techniques or in a glove box. All solvents were distilled under argon with appropriate drying reagents (sodium or calcium hydride). $[\{RuCl_2(CO)_3\}_2]$, $[RuCl_2(\eta^4\text{-cod})]_n$, and $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ were obtained commercially, and used without further purification. $[Ru(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2]$,[15] $[Ru(\eta^4\text{-cod})(\eta^6\text{-cot})]$,[22] $[Ru(\eta^5\text{-}C_8H_{11})(\eta^5\text{-}C_6H_5O)]\cdot PhOH$,[18] $[RuH_2(PPh_3)_4]$,[23] $[RuHCl(CO)(PPh_3)_3]$,[24] $[RuCl_2(PPh_3)_3]$,[25] and $[Cp^*RuCl(\eta^4\text{-cod})]$[26] were prepared as described in the literature. Styrene derivatives **1a**–**d** were obtained commercially and used without further purification. The spectral data of **2a**,[27] **2c**,[28] **4a**,[28] **4b**,[29] and **4c**[30] were consistent with those reported previously. New compounds, **2b** and **2d**, are characterized below.

Ruthenium-catalyzed dimerization of styrenes: A mixture of the styrene derivative (**1**) (2.0 mmol), $[Ru(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2]$ (0.10 mmol), 1-octanol (0.50 mmol) or 1-propanol (6.0 mmol), and mesitylene (0.50 mL) was placed in a two-necked 20-mL pyrex flask equipped with a magnetic stirring bar and a reflux condenser under a flow of argon. The reaction was carried out at 80–110 °C for 24 h with stirring in an argon atmosphere (balloon). After the reaction mixture was cooled, the products were analyzed by GLC, and isolated by Kugelrohr distillation, flash column chromatography on silica gel (hexane/ethyl acetate 95:5), and/or recycling preparative HPLC.

Ruthenium-catalyzed co-dimerization of styrenes with ethylene: A mixture of the styrene derivative **1** (2.0 mmol), $[Ru(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2]$ (0.10 mmol), 1-propanol (6.0 mmol), and mesitylene (0.50 mL) was placed in a 50-mL stainless-steel autoclave equipped with a glass liner and a magnetic stirring bar under a flow of argon. Ethylene was then pressurized to 40 atm at room temperature, and the mixture was magnetically stirred at 130 °C for 24 h. After the reaction mixture was cooled, the products were analyzed by GLC, and isolated by Kugelrohr distillation, flash column chromatography on silica gel (hexane/ethyl acetate 95:5), and/or recycling preparative HPLC.

2b: White solid; m.p. 99 °C; b.p. 150 °C (0.10 Torr, Kugelrohr); IR (neat): $\tilde{\nu} = 2915, 2852, 1512, 1445, 969, 837, 798\ cm^{-1}$; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.39$–7.21 (m, 8H), 6.51 (d, $J = 16.0$ Hz, 1H), 6.34 (dt, $J = 7.3$, 16.0 Hz, 1H,), 2.88 (t, $J = 7.8$ Hz, 2H), 2.62 (dt, $J = 7.3$ Hz, 2H), 2.46 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 138.6$, 136.4, 135.1, 134.8, 129.9, 129.0 (2C), 128.9 (2C), 128.9, 128.2, 125.7 (2C), 35.6, 35.1, 21.3, 21.2 ppm; MS (EI) m/z 236 [M^+]. HRMS (FAB with *meta*-nitrobenzyl alcohol): m/z 236.1571 [M+H]$^+$, calcd for $C_{18}H_{20}$: 236.1565.

2d: White solid; m.p. 74 °C, b.p. 130 °C (0.10 Torr, Kugelrohr); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.29$–6.95 (m, 8H), 6.35 (d, $J = 15.6$ Hz, 1H), 6.12 (dt, $J = 6.80$, 16.0 Hz, 1H), 2.75 (t, $J = 8.00$ Hz, 2H), 2.49 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 161.6$ (d, $^1J_{C\text{-}F} = 244$ Hz) 160.9 (d, $^1J_{C\text{-}F} = 241$ Hz), 136.9 (d, $^4J_{C\text{-}F} = 3.3$ Hz), 133.4 (d, $^4J_{C\text{-}F} = 3.4$ Hz), 129.4 (d, $^3J_{C\text{-}F} = 7.4$ Hz, 2C), 129.1, 129.0, 129.0, 127.1 (d, $^3J_{C\text{-}F} = 8.3$ Hz, 2C), 115.0 (d, $^2J_{C\text{-}F} = 21.6$ Hz, 2C), 114.8 (d, $^2J_{C\text{-}F} = 20.8$ Hz, 2C), 34.9, 34.8 ppm; MS (EI): m/z 246 [M^+], HRMS (FAB with *meta*-nitrobenzyl alcohol): m/z 244.1067 [M+H]$^+$, calcd for $C_{16}H_{14}F_2$: 244.1064.

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