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Tandem Isomerization/Hydroformylation/Hydrogenation of Internal Alkenes to *n*-Alcohols Using Rh/Ru Dual- or Ternary-Catalyst Systems

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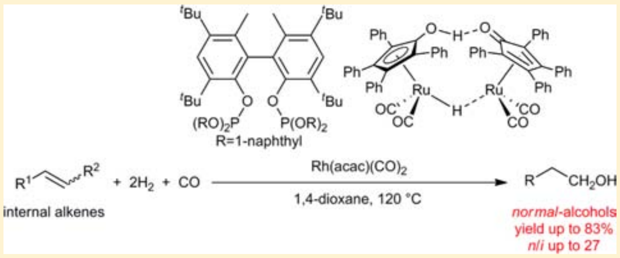
Supporting Information



ABSTRACT: A one-pot three-step reaction, isomerization/hydroformylation/hydrogenation of internal alkenes to *n*-alcohols, was accomplished by employing a Rh/Ru dual-catalyst system. By using a combination of $Rh(acac)(CO)_2$/bisphosphite and Shvo's catalyst, (*Z*)-2-tridecene was converted to 1-tetradecanol in 83% yield with high *normal*/*iso* selectivity (n/i = 12). The method was applicable to other internal alkenes, including functionalized alkenes, such as an alkenol and an alkenoate. Furthermore, addition of a third component, $Ru_3(CO)_{12}$, effectively improved the n/i ratio in the tandem isomerization/hydroformylation/hydrogenation of methyl oleate (from n/i = 1.9 to 4.4). Control experiments revealed that the isomerization was mediated by both Rh and Ru and that the coexistence of Rh and Ru was essential for hydrogenation of aldehyde under H_2/CO.

■ INTRODUCTION

Combination of multiple catalysts in a single vessel to promote multistep conversion of substrates has become widely used in homogeneous catalysis.[1] The tandem hydroformylation/hydrogenation of terminal alkenes (1-alkenes) to *n*-alcohols (1-alkanols) is one of the major research targets of the multicatalyst systems: namely, both the *n*-selective hydroformylation and the subsequent hydrogenation of the resulting *n*-aldehyde by syngas (a mixture of H_2 and CO) in one pot.[2] It would be even more desirable if a mixture of terminal and internal alkenes in a refinery mixture could be directly applied to the *n*-alcohol synthesis.[3] Thus, a tandem three-step reaction consists of the isomerization from internal to terminal alkenes, the *n*-selective hydroformylation, and the aldehyde hydrogenation is an attractive avenue for *n*-alcohol synthesis.

For the first two steps (Scheme 1, reaction **A** + **B**), the isomerization/hydroformylation of internal alkenes to normal aldehydes has been well studied since th e1980s. High n/i ratios (the ratio of normal product to iso product) up to 24 were reported by the researchers of UCC for the hydroformylation of 2-butene to pentanal using a Rh complex of bulky bisphosphite.[4] Since then, continuous efforts have been made to improve the two-step reaction by the development of bidentate phosphorus ligands[5] such as phosphacyclic ligands,[5a] pyrrolyl ligands,[5g] etc.

For the last two steps (Scheme 1, reaction **B** + **C**), that is the tandem normal-selective hydroformylation/hydrogenation of terminal alkenes to *n*-alcohols, Co and Rh systems modified by a trialkylphosphine were reported to be effective.[2a−d] Previously, we reported a Rh/bisphosphine/Ru dual-catalyst system, which afforded *n*-undecanol in 90% yield with n/i = 22 from 1-decene.[2i,j]

For the three-step one-pot conversion of internal alkene to *n*-alcohol (Scheme 1, reaction **A** + **B** + **C**), the cobalt trialkylphosphine catalyst developed by Shell Oil Co. is a well-established system.[6] The current state of the art for the selectivity to alcohols is up to 90% and the n/i ratio is up to 9 with high catalytic activity for a mixture of internal decenes.[6c] This process is also efficient in terms of easy catalyst separation and low cost of catalytic components. The process is industrially operated on a large scale and is the most preferred method to obtain linear aliphatic alcohols ($>C_5$). Few other examples have been reported, but the n/i ratios are insufficient (n/i up to 5.3).[2k−o] Here we report a highly *n*-selective three-step one-pot reaction, isomerization/hydroformylation/hydrogenation to produce *n*-alcohols from various internal alkenes using a Rh/bisphosphite/Ru dual-catalyst system, where Rh and Ru cooperatively work in both the isomerization and hydrogenation steps. Furthermore, addition of a third catalyst accelerated the isomerization process further to yield alcohols in a higher n/i ratio when methyl oleate was employed as a substrate.

■ RESULTS AND DISCUSSION

Isomerization/Hydroformylation/Hydrogenation of (*Z*)-2-Decene and (*Z*)-2-Tridecene Catalyzed by Rh/Phosphorus Ligands/Shvo's Catalyst System. First, the

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Scheme 1. One-Pot Isomerization/Hydroformylation/Hydrogenation of Internal Alkene to Normal Alcohol

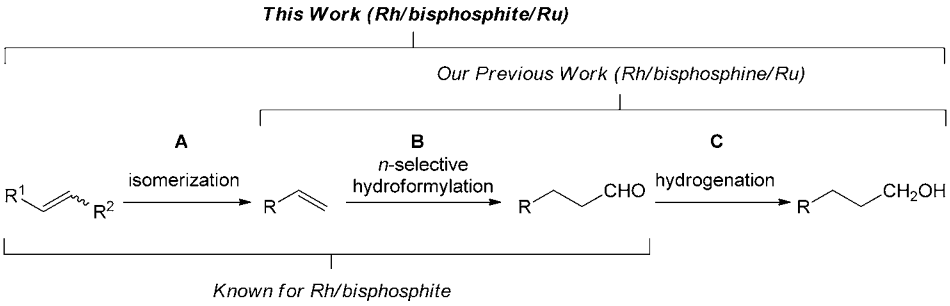
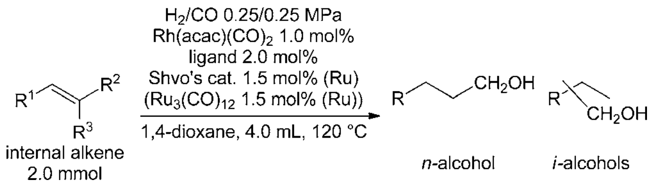


Table 1. Isomerization/Hydroformylation/Hydrogenation of Internal Alkenes Catalyzed by Rh/Phosphorus Ligand/Shvo's Catalyst[a]



run	alkene	ligand	time (h)	conversn (%)	total n/i[b]	alcohol yield (%)		aldehyde yield (%)		direct hydrogenation of C=C (%)	total others (%)[e]
						n	i[c]	n	i[d]		
1	(*Z*)-2-decene	PPh_3 (4.0 mol %)	36	47	0.8	4.8	8.1	11	13	nd[f]	1.0
2	(*Z*)-2-decene	$P(OPh)_3$ (4.0 mol %)	36	94	0.7	24	38	8.0	6.5	nd[f]	0.4
3	(*Z*)-2-decene	XANTPHOS	36	88	1.3	35	27	4.0	2.4	nd[f]	5.7
4	(*Z*)-2-decene	BISBI	36	42	0.4	6.0	19	2.6	4.0	6.0	trace
5	(*Z*)-2-decene	A4N3	36	99	18	75	4.2	3.5	0.2	4.8	trace
6	(*Z*)-2-tridecene	A4N3	36	100	12	83	7.1	trace	trace	6.7	2.6
7	1-octene	A4N3	18	100	40	24	0.6	59	1.5	5.5	4.4
8	(*Z*)-2-octene	A4N3	18	100	27	34	1.5	49	1.5	5.7	1.7
9	(*E*)-2-octene	A4N3	18	100	17	45	2.3	16	1.2	5.0	6.4
10	(*E*)-4-octene	A4N3	18	100	16	46	3.0	17	0.9	4.4	8.2
11	1-methylcyclohexene	A4N3	36	37[e]		trace	19	trace	trace	trace	6.3
12	2-methylstyrene (*E*:*Z* = 1.8:1.0)	A4N3	36	100[g]	4.9	69[g]	14	trace	trace	6.6[e]	7.7
13	(*Z*)-6-nonen-1-ol	A4N3	36	100[g]	9.3	62[h]	6.7	trace	trace	24[e]	5.0
14	(*Z*)-6-nonenyl acetate	A4N3	36	100[g]	4.6	65[g]	14	trace	trace	6.6[e]	12
15	methyl oleate	A4N3	36	86[g]	1.9	37[h]	19[g]	5.0[g]	3.0[g]	23[i]	nd[j]
16[k]	(*Z*)-2-decene	A4N3	36	100	23	71	3.1	1.0	trace	7.7	3.7
17[k]	methyl oleate	A4N3	36	93	4.4	53[h]	12[g]	trace	trace	29[i]	nd[j]

[a] Conditions: alkene 2.0 mmol, H_2 0.25 MPa, CO 0.25 MPa, $Rh(acac)(CO)_2$ 1.0 mol %, ligand 2.0 mol %, Shvo's catalyst 1.5 mol % (based on Ru atom), 1,4-dioxane 4.0 mL, 120 °C. Conversion is defined as consumption of the C=C bond. Yields were determined by gas chromatography using dodecane or tridecane as an internal standard unless otherwise mentioned. [b] Total n/i = ((yield of *n*-alcohol) + (yield of *n*-aldehyde))/((yield of *i*-alcohols) + (yield of *i*-aldehydes)). [c] Total yield of *i*-alcohols estimated by GC by comparing the peak area with that of *n*-alcohol. [d] Total yield of *i*-aldehydes estimated by GC by comparing the peak area with that of *n*-aldehyde. [e] Yields were estimated by GC by comparing the peak area with that of *n*-alcohol. [f] Could not be determined because of the overlapping of the peak with those of isomerized alkenes. [g] Determined by ^1H NMR using 1,3,5-trimethoxybenzene or 1,1,2,2-tetrachloroethane as internal standard. [h] Isolated yield by silica gel column chromatography. [i] NMR yield after rough separation by silica gel column chromatography. [j] Minor uncharacterized signals were found in the ^1H NMR spectrum of the crude mixture. [k] $Ru_3(CO)_{12}$ 1.5 mol % (based on Ru atom) was added as an extra catalyst.

reaction of (*Z*)-2-decene with syngas was examined in the presence of $Rh(acac)(CO)_2$, Shvo's catalyst,[7] and various phosphorus ligands (runs 1−5 of Table 1 and Figure 1). The use of PPh_3 resulted in a low conversion of (*Z*)-2-decene to *n*-alcohol with a low n/i ratio (4.8%, total n/i of alcohol and aldehyde was 0.8, run 1). With $P(OPh)_3$, the conversion of alkene was improved but the n/i ratio remained low (24% *n*-alcohol yield, n/i = 0.7, run 2). Both the yield of *n*-alcohol and the n/i ratio stayed low with bisphosphines XANTPHOS[8] (35%, n/i = 1.3, run 3) and BISBI[9] (6.0%, n/i = 0.4, run 4), which are known to be effective for *n*-selective hydroformylation of terminal alkenes. In sharp contrast, a significant increase of *n*-alcohol yield and n/i was observed with the bulky bisphosphite ligand A4N3[10] (75%, n/i = 18, run 5). These trends well reflect the fact that the Rh/bisphosphite system is generally more effective for the conventional two-step reaction,

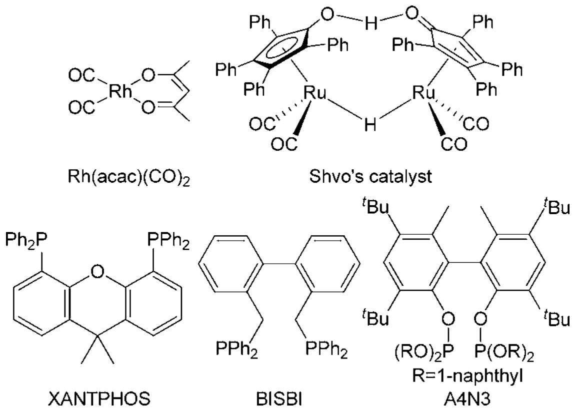


Figure 1. Catalyst components used in this work.

isomerization/hydroformylation (Scheme 1, reaction **A** + **B**) in comparison to Rh/phosphine or Rh/monophosphite systems.[4,5]

In runs 1−5 of Table 1, the sum of all the products did not match the alkene conversion, due to the volatility of the starting material, (*Z*)-2-decene. This was not problematic when (*Z*)-2-tridecene was employed, as demonstrated in run 6 (>99% mass recovery, 83% *n*-alcohol yield, *n*/*i* = 12).

Isomerization/Hydroformylation/Hydrogenation of Other Internal Alkenes Catalyzed by Rh/A4N3/Shvo's Catalyst System. The reaction was further applied to octene isomers (Table 1, runs 7−10). In order to compare the difference in reactivity, the reaction was stopped at 18 h. As for *n*/*i* selectivity, 1-octene was converted into the corresponding alcohols and aldehydes with the highest value (*n*/*i* = 40), followed by (*Z*)-2-octene (*n*/*i* = 27), (*E*)-2-octene (*n*/*i* = 17), and (*E*)-4-octene (*n*/*i* = 16). Assuming that the (*Z*)-2-octene coordinates to the metal catalyst more easily than (*E*)-2-octene to undergo isomerization, the trend may be interpreted that the substrate whose isomerization to the terminal alkene is more facile tends to give the higher *n*/*i* selectivity. In contrast, the yield of the obtained *n*-alcohol resulted in a completely opposite trend. The highest *n*-alcohol yields were recorded for (*E*)-2-octene and (*E*)-4-octene (45 and 46%), followed by (*Z*)-2-octene (34%) and 1-octene (24%). Those yields reflect the reaction rate from the *n*-aldehyde, nonanal, to the *n*-alcohol, 1-nonanol. One possible explanation of the phenomenon is the inhibition of hydrogenation by alkenes. Terminal or (*Z*)-alkenes may more preferably coordinate to the Ru because of their smaller steric repulsion with the other ligands on the Ru, and that interferes with the coordination of dihydrogen, which is required for the generation of the active species of hydrogenation.

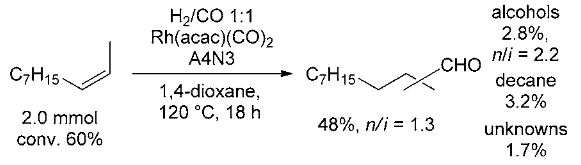
The scope and limitation were investigated with the optimized conditions (Table 1, runs 11−15). A trace amount of *n*-alcohol was obtained from 1-methylcyclohexene accompanied by *iso*-alcohols (19%) probably due to slow isomerization of the trisubstituted cyclic alkene (run 11). A substrate with a conjugated C═C bond, *β*-methylstyrene, was transformed to an *n*-alcohol as a major product (69%, run 12). An internal alkenol and its ester, (*Z*)-6-nonen-1-ol and (*Z*)-6-nonenyl acetate (runs 13 and 14), were converted to *n*-alcohol with moderate yields (62 and 65%) and *n*/*i* ratios (9.3 and 4.6). Finally, methyl oleate, which is a potential renewable chemical feedstock,[11] was tested as a substrate. The *n*-alcohol was given as a major product (37%, *n*/*i* = 1.9) but the direct hydrogenation of the C═C bond took place as a major problematic side reaction. A similar tendency was previously reported in the Rh-catalyzed isomerization/hydroformylation of methyl oleate.[5j]

Consideration of the Selectivity-Determining Step and Addition of Isomerization Catalyst. A selectivity-determining step was speculated by the following control experiment. When the three-step isomerization/hydroformylation/hydrogenation of (*Z*)-2-tridecene was stopped before complete conversion, 1-tridecene was not observed by ^{1}H NMR spectroscopy (see the Supporting Information), which indicated that the rate of hydroformylation of 1-tridecene (reaction **B**, Scheme 1) is much faster than the in situ formation of 1-tridecene by isomerization (reaction **A**, Scheme 1). Since hydroformylation of internal alkenes affords *iso*-aldehydes, the products' *n*/*i* ratios are dependent on the relative rate of isomerization (**A**) over the direct hydroformylation of internal alkenes.

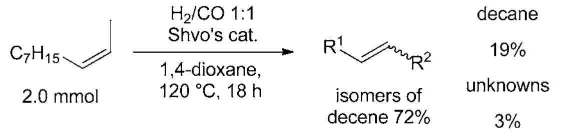
On the basis of this assumption, several catalysts known to catalyze alkene isomerization were tested as an extra additive to improve the *n*/*i* ratio using (*Z*)-2-decene as a model

Scheme 2. Control Experiments To Elucidate the Role of Each Catalyst Component[a]

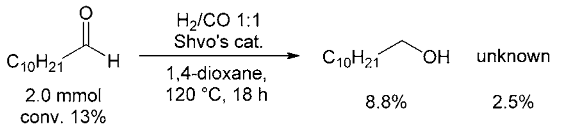
a) Isomerization/hydroformylation of (*Z*)-2-decene by Rh/A4N3



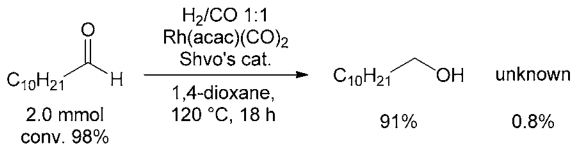
b) Isomerization of (*Z*)-2-decene by Shvo's catalyst



c) Hydrogenation of *n*-undecanal by Shvo's catalyst



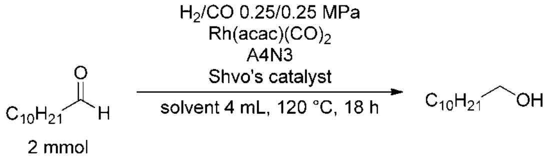
d) Hydrogenation of aldehyde by Rh(acac)(CO)$_2$/Shvo's catalyst



Conditions: Substrate 2.0 mmol, 1,4-dioxane 4.0 mL, H_2 0.25 MPa, CO 0.25 MPa, 120 °C, 18 h. a) Rh(acac)(CO)$_2$ 1.0 mol%, A4N3 2.0 mol%. b), c) Shvo's catalyst 1.5 mol% (Ru). d) Rh(acac)(CO)$_2$ 1.0 mol%, Shvo's catalyst 1.5 mol% (Ru).

[a] Conditions: Substrate 2.0 mmol, 1,4-dioxane 4.0 mL, H_2 0.25 MPa, CO 0.25 MPa, 120 °C, 18 h. a) Rh(acac)(CO)$_2$ 1.0 mol %, A4N3 2.0 mol %. b), c) Shvo's catalyst 1.5 mol % (Ru). d) Rh(acac)(CO)$_2$ 1.0 mol %, Shvo's catalyst 1.5 mol % (Ru).

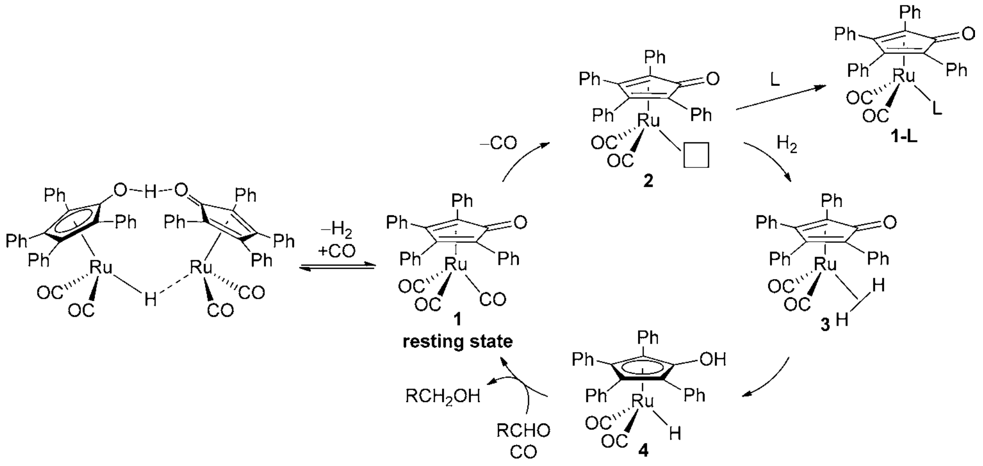
Table 2. Hydrogenation of *n*-Undecanal by Various Combinations of Catalyst Components



run	$Rh(acac)(CO)_2$ (mol %)	A4N3 (mol %)	Shvo's cat. (mol % (Ru))	conversn (%)	*n*-alcohol (%)	other deviations from run 1
1	0	0	2.0	13	8.8	
2	1.5	0	2.0	98	91	
3	1.5	2.0	2.0	96	85	
4	1.5	0	0	13	7.5	
5	0	2.0	2.0	22	7.9	
6	0	0	2.0	98	85	$[Rh(coe)_2Cl]_2$ 1.0 mol %
7	1.5	0	0	34	22	tetraphenylcyclopentadienone 1.0 mol %
8	1.5	0	0	35	8.2	$Ru_3(CO)_{12}$ 2.0 mol % (Ru)
9	0	0	2.0	91	79	DMA used as a solvent

[a] Conditions: undecanal 2.0 mmol, H_2 0.25 MPa, CO 0.25 MPa, 1,4-dioxane 4.0 mL, 120 °C, 18 h. Yields were determined by gas chromatography using dodecane as an internal standard.

Scheme 3. Proposed Reaction Mechanism of Hydrogenation of Aldehyde by Shvo's Catalyst under H_2/CO Pressure[2j] and Trap of Coordinative Unsaturated Species 2 by Another Ligand L



substrate.[12] As a result, $Ru_3(CO)_{12}$ was found to improve the *n*/*i* ratio, while maintaining the yield of *n*-alcohol (*n*/*i* = 23 in run 16 compared to 18 in run 5 of Table 1). Improvement in the *n*/*i* ratio was more prominent when methyl oleate was employed as a substrate (*n*/*i* = 4.4 in run 17 compared to 1.9 in run 15 of Table 1), which is the highest *n*/*i* even for the previous reports on the two-step isomerization/hydroformylation reaction of fatty acids.[5j] As a result, the yield of *n*-alcohol went up to 53%.

Studies on the Cooperative Interaction between the Rh and Ru Catalysts. In order to elucidate the roles played by each catalyst component, the control experiments shown in Scheme 2 were carried out. Some synergetic effects of the multiple catalysts were suggested in addition to the major role of each catalyst, namely isomerization/hydroformylation by Rh/A4N3 and hydrogenation by Shvo's catalyst. The use of Rh/A4N3 in the absence of Shvo's catalyst resulted in isomerization/hydroformylation of (*Z*)-2-decene to undecanal with a much lower *n*/*i* value in comparison to that for the one-pot reaction (*n*/*i* = 1.3 in Scheme 2a in comparison to *n*/*i* = 18 in run 5 of Table 1). This may be explained by the fact that Shvo's catalyst contributed to alkene isomerization to some extent (Scheme 2b). The hydrogenation of undecanal by Shvo's catalyst was also examined under H_2/CO in the absence of Rh/A4N3 (Scheme 2c). Notably, the rate of aldehyde conversion was much lower (13% in 18 h). On the other hand, complete conversion of aldehyde was observed in the presence of a catalytic amount of $Rh(acac)(CO)_2$ (Scheme 2d). This result indicates the cooperativity of Shvo's catalyst and $Rh(acac)(CO)_2$ in the hydrogenation under H_2/CO.

By the control experiments, the coexistence of Shvo's catalyst and Rh(I) was confirmed to be essential and sufficient. Hydrogenation of undecanal was performed under various conditions (Table 2). The results shown in runs 1 and 2 are those of Scheme 2c,d, respectively. By the mixture of $Rh(acac)(CO)_2$, A4N3, and Shvo's catalyst, which is similar to the real catalytic reaction, high conversion was observed (run 3). On the other hand, with only $Rh(acac)(CO)_2$ or a combination of Shvo's catalyst and A4N3, the reaction resulted in low conversions (run 4 and 5). These results indicate that the coexistence of $Rh(acac)(CO)_2$ and Shvo's catalyst is essential for high conversion. Acetylacetone, which is released by the hydrogenolysis of Rh(acac) to Rh−H, is innocent because Shvo's catalyst with $[Rh(coe)_2Cl]_2$ was also effective (run 6). In other possibilities, the enhanced activity might have been derived from a cooperative effect of Rh with free tetraphenylcyclopentadienone or Ru carbonyl complex ($Ru_x(CO)_y$), which could be generated by the dissociation of tetraphenylcyclopentadienone from the Ru center of Shvo's catalyst and the coordination of CO to the resulting Ru. However, neither $Rh(acac)(CO)_2$ with tetraphenylcyclopentadienone nor $Rh(acac)(CO)_2$ with $Ru_3(CO)_{12}$ exhibited high activity (runs 7 and 8). These facts in runs 6–8 could be interpreted by the notion that ligands on the Rh precursor do not make a significant difference but coordination of tetraphenylcyclopentadienone to Ru is essential. The cooperativity between the Rh and Ru catalysts found in this three-step reaction is in contrast to our previous studies on the two-step reaction, hydroformylation/hydrogenation.[2j] In our previous report, when the hydrogenation of undecanal was carried out under 2.0 MPa of H_2/CO in DMA as solvent at 120 °C, Shvo's catalyst and a $Rh(acac)(CO)_2$/XANTPHOS/Shvo's catalyst mixture exhibited quite similar activity. The difference was ascribed to the difference in solvent effects, because rapid hydrogenation took place in DMA without assistance by Rh (run 9).

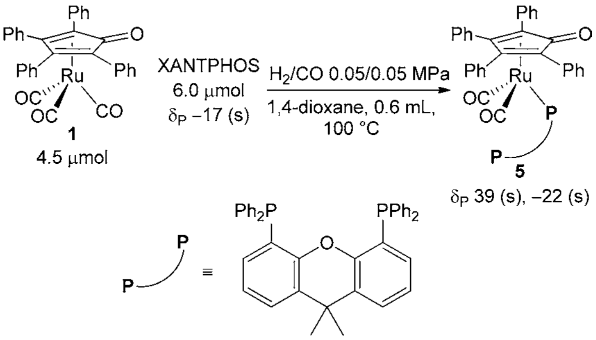
In our previous report, the reaction mechanism of the hydrogenation of undecanal by Shvo's catalyst was proposed as described in Scheme 3. Since **1** was quantitatively obtained by treatment of a solution of Shvo's catalyst under H_2/CO pressure, **1** is suggested to be the resting state. Successive loss of CO to form **2** and coordination of dihydrogen gives the σ-dihydrogen complex **3**.[13] Metal–ligand cooperative activation of dihydrogen affords the active species **4**,[7] and the transfer of the two hydrogen atoms to aldehyde[7e] accompanied by the coordination of CO generates the alcohol and **1**. Assuming the mechanism is the same under the conditions of this work (0.5 MPa of H_2/CO in 1,4-dioxane at 120 °C), the cooperative effect of Rh(I) species would be the acceleration of one of those steps.

By the NMR experiment, Rh was confirmed to accelerate the dissociation of CO from **1** to form **2**, as follows. In order to estimate the rate of generation of **2** from **1**, trapping of **2** with another ligand to give **1-L** was examined in the absence and presence of Rh. Initially, the experiment was tried with A4N3 ligand, but it did not afford a thermodynamically stable Ru complex, probably due to its low basicity and large substituents on the phosphorus atoms. Alternatively, the experiment was carried out by using XANTPHOS as a trapping agent. The reaction of **1** with XANTPHOS (1.5:2 molar ratio) in 1,4-dioxane under 0.1 MPa of H_2/CO at 100 °C was monitored by ^{31}P NMR spectroscopy (Scheme 4). During the reaction, only XANTPHOS and κ^1-xantphos complex **5** were observed by ^{31}P NMR, and the reaction irreversibly proceeded to form **5** quantitatively from **1**. The amount of **1** was estimated by assuming the rest of the Ru existed as **1**.[14] The rate equation was estimated as

$$d[\mathbf{1}]/dt = k_1[\mathbf{1}][\text{XANTPHOS}]$$

$$k_1 = 0.48 \pm 0.01 \text{ L mol}^{-1} \text{ min}^{-1}$$

Scheme 4. Reaction of 1 and XANTPHOS under H_2/CO

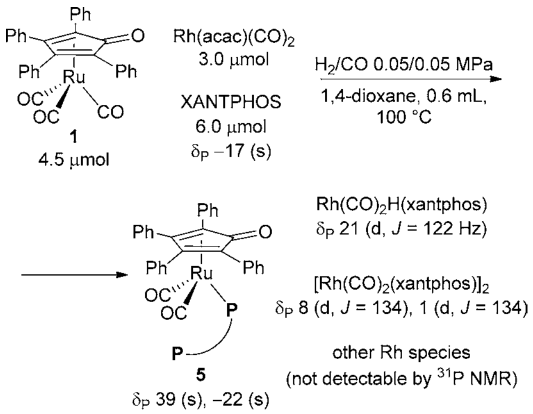


When the exchange of CO of **1** and XANTPHOS was monitored in the presence of Rh, acceleration of the process was observed. A solution of $Rh(acac)(CO)_2$/XANTPHOS/**1** (1:2:1.5 molar ratio) in 1,4-dioxane was treated under 0.1 MPa of H_2/CO at 100 °C. As a result, **5**, XANTPHOS, $Rh(CO)_2H$(xantphos),[8] and $[Rh(CO)_2(\text{xantphos})]_2$[2j] were observed by ^{31}P NMR (Scheme 5). The amounts of $Rh(CO)_2H$(xantphos), and $[Rh(CO)_2(\text{xantphos})]_2$ were constant during the reaction. Therefore, the time-dependent variations observed by ^{31}P NMR spectra reflected only the reaction of **1** and XANTPHOS. In this case, the rate equation was also estimated to be

$$d[\mathbf{1}]/dt = k_2[\mathbf{1}][\text{XANTPHOS}]$$

$$k_2 = 2.5 \pm 0.4 \text{ L mol}^{-1} \text{ min}^{-1}$$

Scheme 5. Reaction of 1 and XANTPHOS under H_2/CO in the Presence of Rh



When the rate constants of the exchange of CO of **1** with XANTPHOS were compared in the absence and presence of Rh ($k_1 = 0.48 \pm 0.01$ L mol^{-1} min^{-1} and $k_2 = 2.5 \pm 0.4$ L mol^{-1} min^{-1}), the reaction was evidently accelerated by a factor of 5 (2.5/0.48) in the presence of Rh. This result suggested that Rh facilitates the dissociation of CO from **1** to **2**, resulting in a higher rate of the generation of active species **4** for the hydrogenation of aldehyde.[15]

■ CONCLUSION

In this work, we developed a Rh/bisphosphite/Shvo's catalyst system for the one-pot isomerization/hydroformylation/hydrogenation of internal alkenes to corresponding homologated *n*-alcohols with high *n*/*i* selectivity. Addition of an extra catalyst for isomerization, $Ru_3(CO)_{12}$, enhanced the *n*/*i* ratio, especially in the reaction of methyl oleate. The roles of each catalytic component were clarified by the control experiments, one of which suggested the cooperativity of Rh and Ru in the hydrogenation of aldehyde under H_2/CO. By a kinetic study of the exchange of the CO of **1** with XANTPHOS, it was suggested that the dissociation of CO from **1** was facilitated in the presence of Rh, and that accelerated the generation of active species for hydrogenation. Although the system of this work is still less effective compared to the currently used cobalt/alkylphosphine system in practical aspects such as catalytic activity, separation, cost, etc., present work would contribute to the future developments of multiple cooperative catalyst systems.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations involving the air- and moisture-sensitive compounds were carried out by using standard Schlenk techniques or a glovebox under argon purified by passing through a hot column packed with BASF catalyst R3-11. Commercially available anhydrous 1,4-dioxane and DMA were distilled and degassed by freeze−pump−thaw before use. Commercially available anhydrous toluene, hexane, and THF were passed through solvent purification columns prior to use. Product yields were determined by a Shimadzu GC-2014 instrument equipped with an InertCap 5MS/Sil capillary column (0.25 i.d., 0.25 μm df, 30 m) using dodecane as an internal standard for (Z)-2-decene and tridecane for all other substrates. NMR spectra were recorded with JEOL JIN-ECP500 and JEOL-ECS400 spectrometers. Chemical shifts are reported in ppm relative to the residual protiated solvent for ^{1}H nuclei and an external standard for ^{13}C ($(CH_3)_4Si$) and ^{31}P (H_3PO_4) nuclei. Data are presented in the following order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. NMR yields were determined by ^{1}H experiments with a 15 s relaxation delay using 1,3,5-trimethoxybenzene or 1,1,2,2-tetrachloroethane as an internal standard. H_2/CO mixed gas (H_2:CO = 49.1:50.9) was purchased from Suzuki-Shoukan and used without further purification. 1-Decene, (Z)-2-decene, 1-octene, (Z)-2-octene, (E)-2-octene, (E)-4-octene, dodecane, tridecane, n-undecanal, 1-methylcyclohexene, (Z)-2-methylstyrene, (Z)-6-nonen-1-ol, (Z)-6-nonenyl acetate, PPh_3, $P(OPh)_3$, and 2,3,4,5-tetraphenylcyclopentadienone were purchased from TCI. Methyl oleate and Rh(acac)$(CO)_2$ were purchased from Aldrich. XANTPHOS,[8] BISBI,[9] Shvo's catalyst,[7e] $Ru_3(CO)_{12}$,[16] [Rh(coe)$_2$Cl]$_2$,[17] (Z)-2-tridecene,[18] and **1**[2j] were prepared by literature procedures. A4N3 was prepared by Mitsubishi Chemicals by a patented procedure.[10] Liquid compounds were degassed by three freeze−pump−thaw cycles before use.

Standard Procedure of Tandem Isomerization/Hydroformylation/Hydrogenation of (*Z*)-2-Decene by a Dual-Catalyst System. In a 50 mL stainless steel autoclave, Rh(acac)$(CO)_2$ (5.2 mg, 20 μmol), phosphorus ligand (40.0 μmol), and the appropriate solvent (1.0 mL) were charged under an argon atmosphere. The autoclave was flushed with H_2/CO and stirred at room temperature for 5 min. A solution of Shvo's catalyst (16.3 mg, 30.0 μmol (based on Ru atom)) in an appropriate solvent (3.0 mL) was prepared in a Schlenk tube, and then the solution was transferred to the autoclave. A mixture of the substrate (Z)-2-decene and dodecane ([1-decene]/[dodecane] = 2.00) was added via syringe (550 μL, ca. 450 mg, ca. 2.0 mmol) into the autoclave. The exact amount of substrate was determined by the change in weight of the syringe before and after addition. The autoclave was pressurized with the appropriate pressure of H_2/CO, and the mixture was stirred at the desired temperature and reaction time. The gas was released after the autoclave was cooled to room temperature, and the crude product was diluted with toluene and analyzed by gas chromatography. Peaks for n-aldehyde and n-alcohol were assigned by comparison with authentic samples. Peaks having retention times close to but shorter than that of n-aldehyde were assigned as i-aldehydes. Peaks having retention time close but shorter than n-alcohol and longer than n-aldehyde were assigned as i-alcohols. Yields of n-undecanal, n-undecanol, and decane and recovery of alkenes were determined by calibration curves using dodecane as an internal standard. Yields of i-aldehydes and i-alcohols were determined by using calibration curves made for n-aldehyde and n-alcohol, respectively. Conversions were defined as consumption of C═C bonds because all decene isomers could potentially be converted to n-alcohols. Details of optimization of the reaction conditions are summarized in Table S1 in the Supporting Information.

Tandem Isomerization/Hydroformylation/Hydrogenation of Octene Isomers, 1-Methylcyclohexene, 2-Methylstyrene, (*Z*)-6-Nonen-1-ol, and (*Z*)-6-Nonenyl Acetate by a Dual-Catalyst System. The experiments were similarly performed except using tridecane in place of dodecane. Products were assigned by ^{1}H NMR and/or accordance of retention time with authentic sample by GC. Yields were determined as follows.

Octene Isomers. Yields of n-alcohol, n-aldehyde, and octane were determined by GC with a calibration curve made with an authentic sample. Yields of i-alcohols and unknown side products were estimated by a calibration curve made for n-alcohol. Yields of i-aldehydes were estimated by a calibration curve made for n-aldehyde.

(Z)-2-Tridecene. The yield of n-alcohol was determined by ^{1}H NMR (δ 3.60 (t, J = 7)) using 1,1,2,2-tetrachloroethane as an internal standard after evaporation of the solvent. Yields of i-alcohols, tridecane, and unknown side products were estimated by GC on comparison of integrations of the peaks with that of n-alcohol. The n/i ratio determined by GC was consistent with the value estimated by ^{1}H NMR spectroscopy.

1-Methylcyclohexene. Yields of n-alcohol, n-aldehyde, and i-aldehydes were trace amounts. Yields of i-alcohols and unknown side products were estimated by GC with a calibration curve made for n-alcohol.

2-Methylstyrene. The E/Z ratio of the commercially available starting material was determined by GC and ^{1}H NMR. The crude mixture was analyzed by ^{1}H NMR and GC to confirm the complete absence of C═C bonds and aldehydes. The yield of n-alcohol was determined by GC with a calibration curve made with an authentic sample. Yields of i-alcohols, n-propylbenzene, and unknown side products were estimated by a calibration curve made for n-alcohol. The determined n/i ratio by GC was consistent with the value estimated by ^{1}H NMR spectroscopy.

(Z)-6-Nonen-1-ol. The crude mixture was analyzed by ^{1}H NMR and GC to confirm the absence of C═C bonds and aldehydes. The n-alcohol was isolated by silica gel column chromatography (hexane:EtOAc = 1:1 → 1:2). Yields of i-alcohols, nonanol, and unknown side products were estimated by GC by comparing integrations of the peaks with that of n-alcohol. The n/i ratio determined by GC was consistent with the value estimated by ^{1}H NMR spectroscopy.

(Z)-6-Nonenyl Acetate. The crude mixture was analyzed by ^{1}H NMR and GC to confirm the absence of C═C bonds and aldehydes. The yield of n-alcohol was determined by ^{1}H NMR (δ 3.64 (t, J = 7 Hz)) using 1,1,2,2-tetrachloroethane as an internal standard after evaporation of the solvent. Yields of i-alcohols, nonanyl acetate, and unknown side products were estimated by GC by comparing integrations of the peaks with that of n-alcohol. The n/i ratio determined by GC was consistent with the value estimated by ^{1}H NMR spectroscopy.

Tandem Isomerization/Hydroformylation/Hydrogenation of Methyl Oleate by a Dual-Catalyst System. The experiment was performed similarly for other substrates. After the gas was released, 1,4-dioxane was removed by evaporation and the resulting solid was analyzed by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard. The recovery of C═C bonds (δ 5.26−5.61 (m)) and the yields of i-alcohols (δ 3.46−3.56 (m)), n-aldehyde (δ 9.76 (t, J = 2)), and i-aldehydes (δ 9.55 (m), and δ 9.53 (d, J = 3)) were determined. After the crude mixture was concentrated, silica gel column chromatography (hexane: Et_2O = 3:2 → 2:3) afforded three fractions (R_f values are those with hexane:Et_2O = 2:3 as an eluent): (1) R_f = 0.3, pure n-alcohol; (2) R_f = 0.9, mixture of isomers of starting material with different positions of C═C bonds and directly hydrogenated product; (3) R_f = 0.35, mixture of i-alcohols and unknown side products. The yield of directly hydrogenated product was determined by a ^{1}H NMR spectrum of the mixture (2). The colorless solid obtained by recrystallization from hot AcOEt solution of fraction (1) was submitted for elemental analysis.

Methyl 19-Hydroxynonadecanoate. To the sample for the ^{1}H NMR experiment was added 1 drop of D_2O to eliminate the signal of H_2O in $CDCl_3$ (s, 1.56 ppm): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.66 (s, 3H), 3.63 (t, J = 8.1, 2H), 2.30 (t, J = 7.4, 2H), 1.65−1.51 (m, 4H), 1.38−1.20 (m, 28H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 174.5 (4°), 63.2 (CH_2), 51.6 (CH_3), 34.3 (CH_2), 33.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2) 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 25.9 (CH_2), 25.1 (CH_2); mp 67 °C; IR (neat, cm^{-1}) 3279 (O−H), 2916 (C−H), 2847 (C−H), 1740 (C=O). Anal. Calcd for $C_{20}H_{40}O_3$: C, 73.12; H, 12.27. Found: C, 72.86; H, 12.43. ^{1}H and ^{13}C NMR spectra are given in the Supporting Information (Figures S1 and S2).

Tandem Isomerization/Hydroformylation/Hydrogenation of Methyl Oleate by a Ternary Catalyst System. In a 50 mL stainless steel autoclave, Rh(acac)$(CO)_2$ (5.2 mg, 20 μmol), A4N3 (42.9 mg, 40.0 μmol), and 1,4-dioxane (1.0 mL) were charged under an argon atmosphere. The autoclave was flushed with H_2/CO (1/1 molar ratio) gas, and the mixture was stirred at room temperature for 5 min. A solution of Shvo's catalyst (16.3 mg 30.0 μmol (based on Ru)) and $Ru_3(CO)_{12}$ (5.3 mg, 20 μmol (based on Ru)) in 1,4-dioxane (3.0 mL) was prepared in a Schlenk tube, and then the solution was transferred to the autoclave. Methyl oleate (680 μL, ca. 2.0 mmol) was added via syringe into the autoclave. The exact amount of substrate was determined by the change in weight of the syringe before and after addition. The autoclave was pressurized with 0.5 MPa of H_2/CO and the mixture stirred at 120 °C for 36 h. The gas was released after the autoclave was cooled to room temperature. Yields were determined as described above.

Isomerization/Hydroformylation of (*Z*)-2-Decene by Rh(acac)$(CO)_2$/A4N3. In a 50 mL stainless steel autoclave, Rh(acac)$(CO)_2$ (5.2 mg, 20 μmol), A4N3 (42.9 mg, 40.0 μmol), and 1,4-dioxane (4.0 mL) were charged under an argon atmosphere. The autoclave was flushed with H_2/CO gas, and a mixture of (*Z*)-2-decene and dodecane ([(*Z*)-2-decene]/[dodecane] = 2.00) was added via syringe (550 μL, ca. 450 mg, (*Z*)-2-decene 2 mmol) into the autoclave. The exact amount of substrate was determined by the change in weight of the syringe before and after addition. The autoclave was pressurized with 0.5 MPa of H_2/CO, and the mixture was stirred at 120 °C for 18 h. The gas was released after the autoclave was cooled to room temperature. Yields were determined similarly as explained above.

Isomerization of (*Z*)-2-Decene by Shvo's Catalyst. In a 50 mL stainless steel autoclave, were placed Shvo's catalyst (16.3 mg, 30.0 μmol), 1,4-dioxane (4.0 mL), and (*Z*)-2-decene. The autoclave was pressurized by 0.5 MPa of H_2/CO, and the mixture was stirred at 120 °C for 18 h. The gas was released after the autoclave was cooled to room temperature. Yields were determined similarly as explained above.

Hydrogenation of *n*-Undecanal by Various Combinations of Catalyst Components. In a 50 mL stainless steel autoclave were placed the appropriate catalyst, solvent (4.0 mL), and a mixture of *n*-undecanal and dodecane as an internal standard ([undecanal]/[dodecane] = 2.00) (640 μL, ca. 510 mg, undecanal 2 mmol). The autoclave was pressurized by 0.5 MPa of H_2/CO, and the mixture was stirred at 120 °C for 18 h. The gas was released after the autoclave was cooled to room temperature. Yields were determined similarly as explained above.

Evidence for the Absence of Terminal Alkene during Isomerization/Hydroformylation/Hydrogenation of (*Z*)-2-Tridecene. The experimental procedure was same as that explained above, except that the reaction was stopped after 6 h. There was no evidence of 1-tridecene (δ 5.86−5.77 (m, 1H), 5.02−4.91 (m, 2H)). The selected region of the obtained NMR spectrum is shown in Figure S3 in the Supporting Information.

Estimation of the Rate of Exchange of CO of 1 with XANTPHOS in the Absence of Rh. In a J. Young valve NMR tube were added solutions of XANTPHOS (0.0300 M in 1,4-dioxane, 200 μL, corresponds to 6.0 μmoL of XANTPHOS), tricarbonyl(2,3,4,5-tetraphenylcyclopentadienone)ruthenium (**1**; 0.0225 M in 1,4-dioxane 200 μL, corresponds to 4.5 μmoL), and 1,4-dioxane (200 μL). The solution was degassed by three freeze−pump−thaw cycles to fill it with 0.1 MPa of H_2/CO and heated in an oil bath at 100 °C. After each period of heating, the solution was analyzed by ^{31}P NMR spectroscopy (256 scans). The singlet at −17 ppm was assigned to XANTPHOS,[8] and resonances at 39 and −22 ppm were assigned to two nonequivalent phosphorus atoms of dicarbonyl(tetraphenylcyclopentadienone)(xantphos-κ^1P)ruthenium (**5**).[2i] The amounts of phosphorus-containing compounds were estimated by the ratio of the integrations of the signals by assuming that the sum of the integrations of all signals corresponded to 12.0 μmol of phosphorus atom. The amount of **1** was estimated by assuming all of the Ru species except **5** was **1**. The time courses of each compound, the plot to determine k_1, and the NMR spectra are shown in the Supporting Information (Figures S4 and S6). The experiment was carried out twice, and k_1 was reported as the mean value and deviation of these two experiments.

Estimation of the Rate of Exchange of CO of 1 with XANTPHOS in the Presence of Rh. In a J. Young valve NMR tube were added solutions of Rh(acac)$(CO)_2$ (0.150 M in 1,4-dioxane, 200 μL, corresponds to 3.0 μmoL of Rh(acac)$(CO)_2$) and XANTPHOS (0.0300 M in 1,4-dioxane, 200 μL, corresponds to 6.0 μmoL of XANTPHOS) under Ar, and the mixture was allowed to stand for 5 min. Then a solution of **1** (0.0225 M in 1,4-dioxane 200 μL, corresponds to 4.5 μmoL) was added. The solution was degassed by three freeze−pump−thaw cycles to fill it with 0.1 MPa of H_2/CO and heated in an oil bath at 100 °C. After each period of heating, the solution was analyzed by ^{31}P NMR spectroscopy (256 scans). The singlet at −17 ppm was assigned to XANTPHOS,[8] and the singlets at 39 and −22 ppm were assigned to two nonequivalent phosphorus atoms of dicarbonyl(tetraphenylcyclopentadienone)(xantphos-κ^1P) ruthenium (**5**).[2i] The doublet at 21 ppm (J = 122) was assigned to dicarbonylhydrido(xantphos)rhodium,[8] and the doublets at 8 (J = 134) and 1 ppm (J = 134) were assigned to dicarbonyl(xantphos)-rhodium dimer.[2j] The amounts of phosphorus-containing compounds were estimated by the ratio of the integrations of the signals by assuming that the sum of the integrations of all the signals corresponded to 12.0 μmol of phosphorus atom. The amount of **1** was estimated by assuming that all of the Ru species except **5** was **1**. The time courses of each compound, the plot to determine k_2, and the NMR spectra are shown in the Supporting Information (Figures S5 and S7). The experiment was carried out twice, and k_2 was reported as the mean value and deviation of these two experiments.

■ ASSOCIATED CONTENT

Supporting Information

Tables and figures giving the entire optimization of catalysts and conditions, screening of isomerization catalysts, NMR spectra, and plots determining rate constants k_1 and k_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) To accelerate isomerization of C═C bonds, extra amounts of $Fe(CO)_5$, $Pd(OTf)_2$, $Ru_3(CO)_{12}$, and Shvo's catalyst were tested. A detailed experimental procedure and results are given in the Supporting Information.

(13) Considering steric repulsion with tetraphenylcyclopentadienone, associative exchange of CO and H_2 is not probable.

(14) It was previously reported[2i] that Shvo's catalyst was quantitatively converted to **1** under H_2/CO pressure in the absence of XANTPHOS, which supports the assumption.

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