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Tandem Hydroformylation/Hydrogenation of Alkenes to Normal Alcohols Using Rh/Ru Dual Catalyst or Ru Single Component Catalyst

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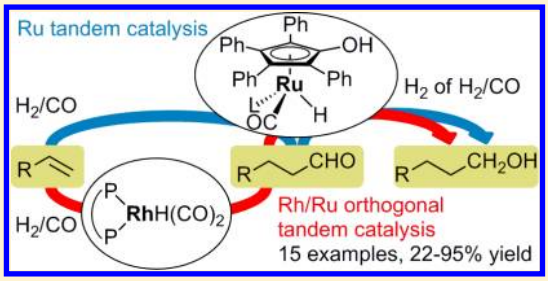
Supporting Information

ABSTRACT: The catalyst system for tandem hydroformylation/hydrogenation of terminal alkenes to the corresponding homologated normal alcohol was developed. The reaction mechanism for the Rh/Ru dual catalyst was investigated by real-time IR monitoring experiments and ^{31}P NMR spectroscopy, which proved the mutual orthogonality of Rh-catalyzed hydroformylation and Ru-catalyzed hydrogenation. Detailed investigation about Ru-catalyzed hydrogenation of undecanal under H_2/CO pressure clarified different kinetics from the hydrogenation under H_2 and gave a clue to design more active hydrogenation catalysts under H_2/CO atmosphere. The solely Ru-catalyzed normal selective hydroformylation/hydrogenation is also reported.

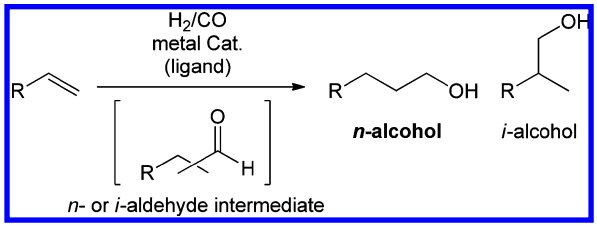


INTRODUCTION

Linear 1-alkanols (*n*-alcohols) are widely used in industry as solvents and precursors of detergents.[1] Direct and selective conversion of terminal alkene into *n*-alcohol by anti-Markovnikov hydration would be an ideal process.[2] In reality, current industrial production of *n*-alcohols mostly employs a multiple-step process consisting of hydroformylation of terminal alkenes, purification of *n*-aldehydes, and then hydrogenation of *n*-aldehydes to *n*-alcohols. One-pot hydroformylation/hydrogenation process would be advantageous because it simplifies the process operation. As another alternative to the anti-Markovnikov hydration, Grubbs et al. reported a tandem Wacker oxidation/hydrogenation of 1-alkenes to *n*-alcohols, very recently.[3]

The tandem hydroformylation/hydrogenation has been investigated for a long time using Co-,[4] Rh-,[5] Ru-,[6] and Pd-based[7] systems (Scheme 1). Although these tandem systems gave a mixture of *n*- and *i*-alcohols in good yields (mostly >90%), a significant amount of alkane was often given as a byproduct. In addition, another problematic issue is the low normal/iso selectivities (n/i < 10) in the hydroformylation step, causing low *n*-alcohol yield (up to 81%). Through those investigations, it was shown to be difficult to achieve the tandem reaction by using only one catalyst.

Scheme 1. Tandem hydrformylation/hydrogenation



Instead of expecting one catalyst to play multiple roles, the use of multiple catalysts in one pot may be a more effective approach to the tandem reaction. Recently, Cole-Hamilton et al.[8] and Breit et al.[9] reported a tandem hydroformylation/hydrogenation catalyst system employing Rh precursor with two ligands giving high *n*-alcohol yield (~90%) with high n/i (>30). In these systems, one ligand is in charge for the Rh-catalyzed *n*-selective hydroformylation, and the other ligand mediates the Rh-catalyzed hydrogenation, respectively. Vogt et al. reported that Rh/XANTPHOS,[10] which was originally reported as *n*-selective hydroformylation catalyst and does not catalyze hydrogenation, can catalyze this tandem reaction (*n*-alcohol 86%, n/i = 11) in a 1:9 mixture of polar organic solvent and water at high temperatures.[11]

In 2010, we reported a Rh/Ru dual system for tandem hydroformylation/hydrogenation, converting 1-decene to *n*-undecanol in over 90% yield (n/i = 22).[12] In the system, we employed Rh/XANTPHOS[10] as a *n*-selective hydroformylation catalyst and Shvo's catalyst[13] as a chemo-selective hydrogenation catalyst. The key to our success could be attributed to the "orthogonality" between each catalyst. Shvo's catalyst was relatively inert in the hydroformylation step compared to the rapid hydroformylation by Rh. Possible side reactions like hydrogenation of 1-decene to decane or isomerization to 2-decenes were not problematic. Also, Shvo's complex maintained hydrogenation activity to aldehyde in the presence of Rh, XANTPHOS, and even CO. A control experiment analyzing catalyst solution by ^{31}P NMR spectroscopy showed no evidence

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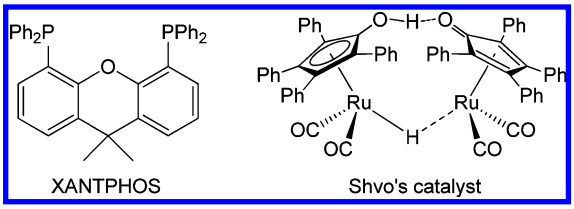
for the presence of Rh−Ru cluster, which also supported the orthogonality of these catalysts.

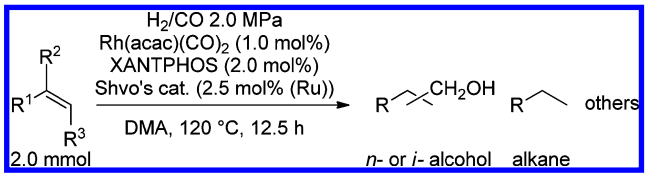
In this work, we report the scope and limitation of the Rh/Ru dual catalyst system aiming at the production of linear α,ω-diols. Terminal alkenes having hydroxyl or various functional groups were converted to the corresponding homologated linear alcohols in good yields. Also, a kinetic study using a real-time IR monitoring system and analysis of catalyst solution by ^{31}P NMR spectroscopy proved the mutual orthogonality of our catalyst system and gave a clue to design a new hydrogenation catalyst more tolerant to CO. Furthermore, here we report a Ru-catalyzed tandem *normal*-selective hydroformylation/hydrogenation. Although the catalytic activity is much lower than the Rh/Ru system, the Shvo's catalyst itself mediated both hydroformylation of 1-alkene and the subsequent hydrogenation of aldehyde to alcohol.



RESULTS AND DISCUSSION

Substrate Scope. Among various *n*-alcohols, linear α,ω-diols are of industrial products utilized as monomers for polyurethanes, polyesters, etc.[14] Our Rh/XANTPHOS/Shvo's catalyst system was successfully applied to the diols syntheses. The results are summarized in the Table 1. The previously reported data for the 1-decene are cited as run 1 in ref 12. When allyl alcohol was treated under the same conditions, the corresponding homologated alcohol, that is, 1,4-butandiol was obtained in a low yield (31%, run 2). A significant amount of propanol was given due to the direct hydrogenation of allyl alcohol (roughly estimated as 20%). While Shvo's complex is less active for the hydrogenation of a C═C double bond, isomerization of allyl alcohol to propanal allows rapid hydrogenation of the resulting C═O double bond affording 1-propanol.[15] Moreover, the hydroformylation product 4-hydroxybutanal formed a five-membered ring cyclic hemiacetal, which underwent dehydrogenation to produce thermodynamically stable γ-butyrolactone. On the other hand, allyl acetate, which corresponds to the protected form of ally alcohol was successfully converted to 4-hydroxybutyl acetate in higher yield (78%, run 3) because both isomerization of C═C to C═O and formation of hemiacetal were suppressed. In the same way, homoallyl alcohol, which is susceptible to formation of six-membered ring cyclic acetal gave 1,5-pentandiol in 75% and δ-valerolactone in 11% yields (run 4), and homoallyl acetate gave 5-hydroxypentyl acetate in 87% yield without any significant byproducts (run 5). An even longer alcohol 4-pentene-1-ol was converted to 1,6-hexanediol with excellent yield (95%) without any byproduct (run 6). Functional group tolerance was demonstrated in runs 7−11. Alkenes having THPO (80%, run 7), benzyloxy (81%, run 8), TBSO (80%, run 9), 1,3-dioxolan-2-yl (79%, run 10), and phenylcarbamate (75%, run 11) groups gave corresponding homologated *n*-alcohol with

Table 1. Hydrofromylation/Hydrogenation of Various 1-Alkenes Catalyzed by Rh/Ru[a]



run	R^1, R^2, R^3	alcohols *n* (%)	alcohols *i* (%)[b]	*n*/*i*	alkane (%)	others[c] (%)
1	C_8H_{17}, H, H	90	4.1	22	1.4	internal alkenes (1.9)
2	$HOCH_2$, H, H	31	3.5	8.9	20[d]	γ-butyrolactone (10)[d] high boiling products (4)[d,e]
3	$AcOCH_2$, H, H	78	trace	>100	1.9	butanol (9) isobutanol (10)[b]
4	$HO(CH_2)_2$, H, H	75	2.4	32	4.5	cyclic acetals (3)[f] δ-valerolactone (11)[f]
5	$AcO(CH_2)_2$, H, H	87	5.6	16	4.5	nd
6	$HO(CH_2)_3$, H, H	95	2.9	33	4.0	none
7	$THPO(CH_2)_4$[g], H, H	80[f]	5.0[f]	16	nd	*n*-aldehyde (4)[f] internal alkenes (2)[f]
8	$PhCH_2O(CH_2)_4$, H, H	81[f]	4.1[d]	20	nd	internal alkenes (2)[f] formates (6)[f]
9	$TBSO(CH_2)_4$[h], H, H	80[f]	3.7[f]	22	nd	formate (4)[f]
10	(1,3-dioxolan-2-yl)$(CH_2)_8$, H, H	79[f]	4.2[f]	19	nd	formate (3)[f]
11	$PhNHCO_2(CH_2)_4$, H, H	75[f]	4.9[f]	15	nd	nd
12	cyclohexyl, H, H	87[f]	4.9[f]	18	nd	nd
13	C_7H_{15}, CH_3, H,	62[f]	trace	>50	nd	starting material (15)[f] internal alkenes (8)[f]
14	C_7H_{15}, H, CH_3	22[i]	34	0.6	nd	internal alkenes (34) aldehydes (4.2)
15	Ph, H, H	60	39	1.5	0	none

[a]Reaction conditions: alkene, 2.0 mmol; $Rh(acac)(CO)_2$, 20 μmol; XANTPHOS, 40 μmol; Shvo's cat, 50 μmol (based on mol of Ru atom); DMA, 4.0 mL; H_2, 1.0 MPa; CO, 1.0 MPa; 12.5 h. The yields in the table were determined by GC analysis with dodecane or tridecane as internal standard otherwise mentioned. *n*/*i* = (mol of *n*-alcohol)/(mol of *i*-alcohols). The yields of aldehydes were trace otherwise mentioned. nd = not determined [b]Yields were determined by using calibration curve for *n*-alcohol. [c]Number in the parentheses is the yield of the products. [d]Yields were roughly estimated by GC, comparing the integration of the peak with that of *n*-alcohol and corrected based on the number of carbon. [e]Probably acetals or aldol products. [f]Yield was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard. [g]THP = 2-tetrahydropyranyl. [h]TBS = *tert*-butyldimethylsilyl [i]Yield of *n*-undecanol.

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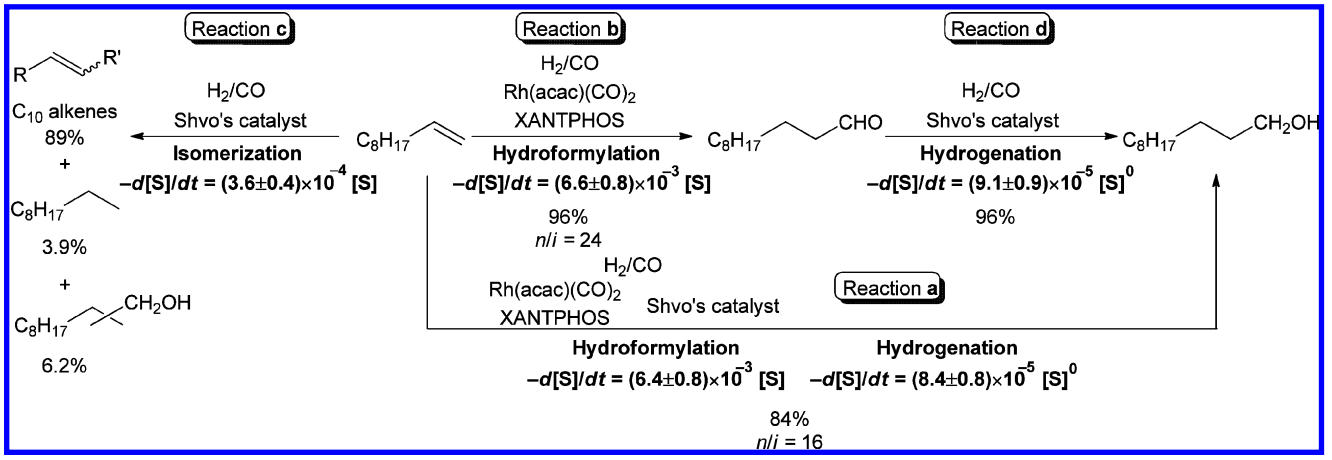
Scheme 2. Summary of Observed Reaction Rate As a Function of Substrate for Each Step[a]



[a][S]: concentration of substrate in each reaction.

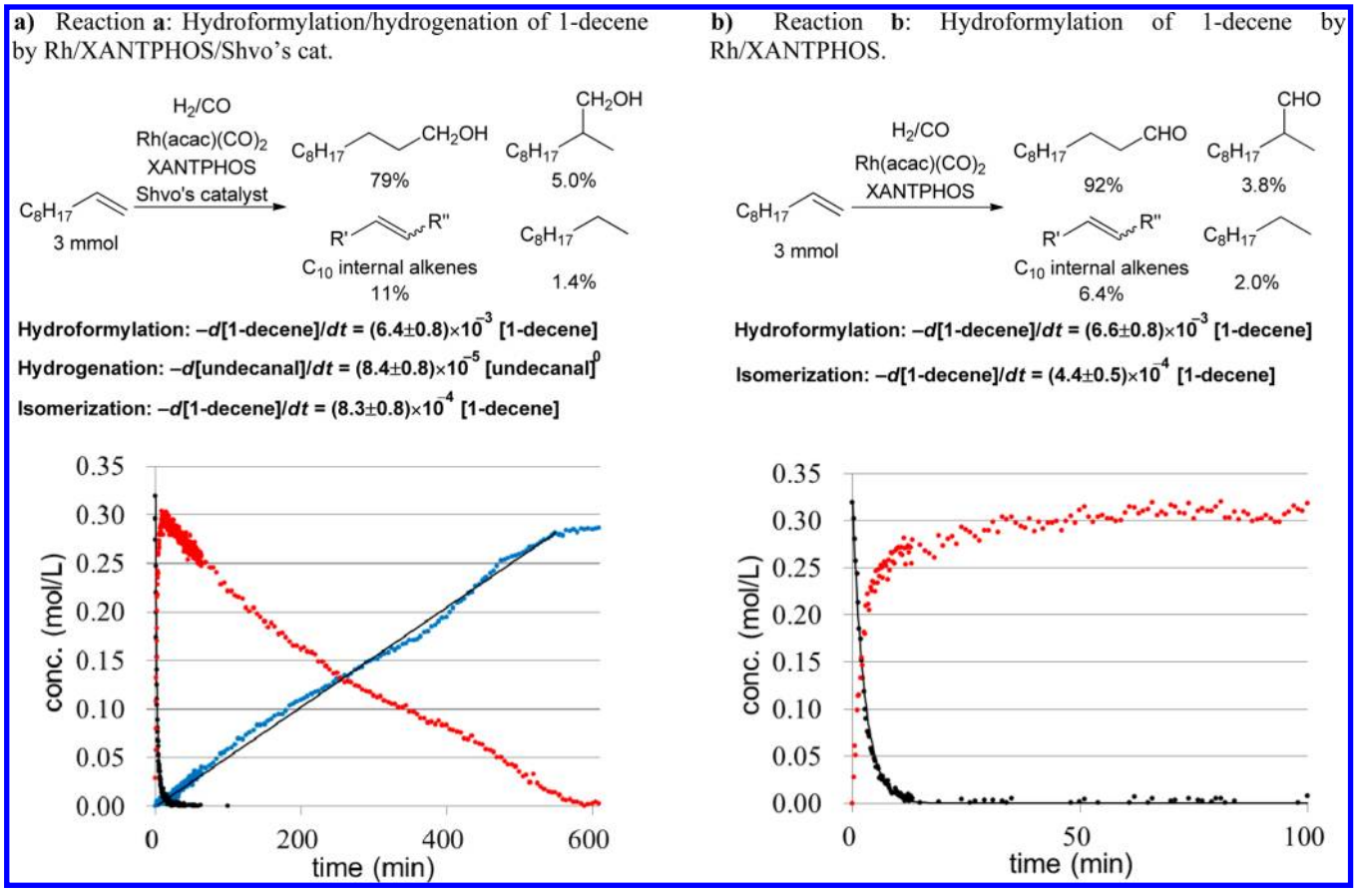


Figure 1. Time course of substrate and products concentration in the hydroformylation catalyzed by Rh/XANTPHOS in the presence of Shvo's catalyst (a) and in the absence (b) monitored by real-time IR spectra. Black dot: 1-decene, red dot: *n*- and *i*-aldehyde, and blue dot: *n*- and *i*-alcohol. Decay of 1-decene until 95% conversion was fitted with first-order equation. Formation of *n*- and *i*-alcohol was fitted with zero-order reaction. Black line shows the fitted functions. Common conditions: DMA, 9 mL; H_2, 1.0 MPa; CO, 1.0 MPa. (a) 1-decene, 3 mmol; $Rh(acac)(CO)_2$, 50 μmol; XANTPHOS, 100 μmol; Shvo's cat, 125 μmol (based on mol of Ru atom). (b) 1-decene, 3 mmol; $Rh(acac)(CO)_2$, 50 μmol; XANTPHOS, 100 μmol.

good yield and similar *n*/*i* with 1-decene. As other examples, vinylcyclohexane and 2-methylnonene gave *n*-alcohol in 87 and 62% yields, respectively (run 12 and 13). An internal alkene, (*Z*)-2-decene, was converted to *n*-undecanol (22% run 14) via isomerization to 1-decene, *n*-selective hydroformylation and hydrogenation. However the formation of *i*-alcohol via direct hydroformylation of the internal C═C bond flowed by hydrogenation was still dominant (34% run 14). Styrene was quantitatively converted to alcohols, but low *n*/*i* (1.5) was observed because the formation of *iso*-aldehyde is intrinsically preferable in the hydroformylation of styrene (run 15).[10]

When compared with precedents of the tandem hydroformylation/hydrogenation using Rh as a singular catalyst by Cole-Hamilton[8] and by Breit,[9] the present system showed

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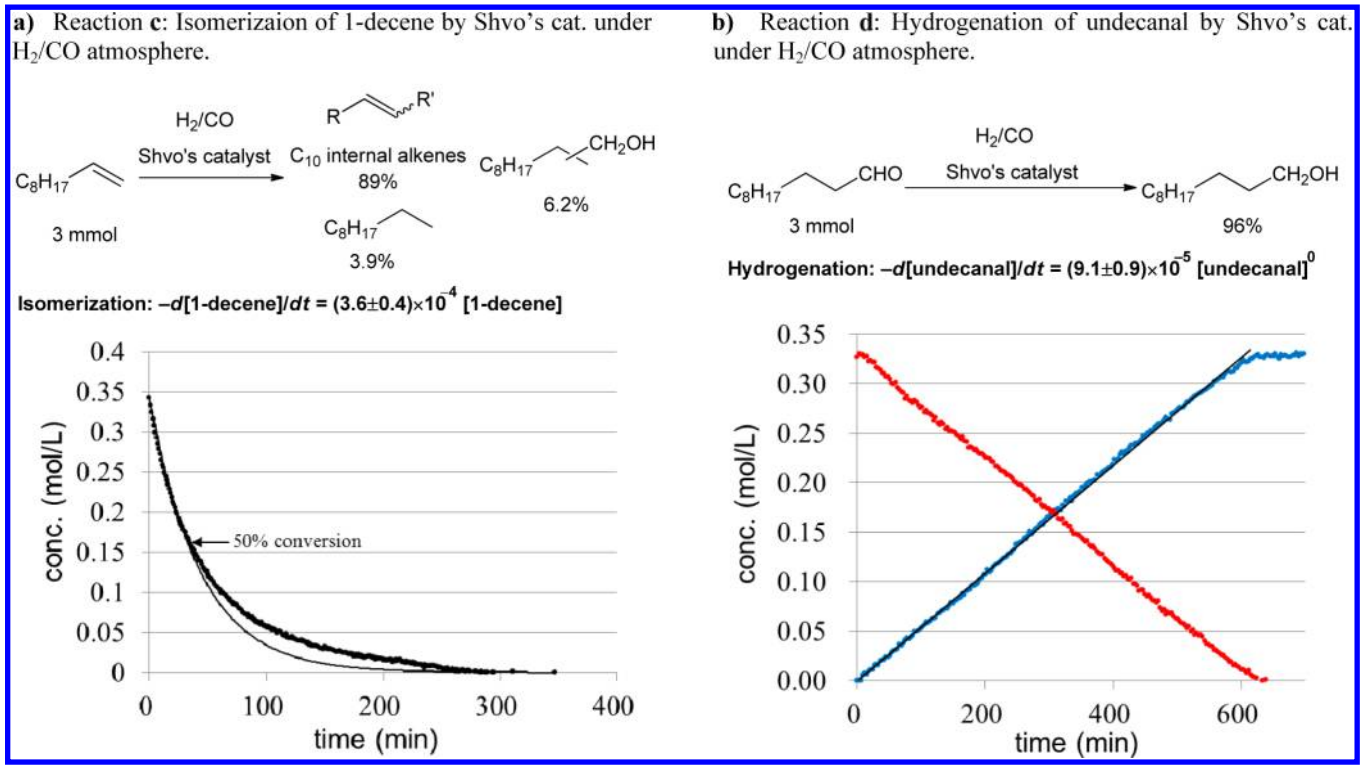

Figure 2. (a) Time course of 1-decene consumption in the presence of Shvo's catalyst monitored by real-time IR spectra. (b) Time course of undecanal and undecanol concentration in the presence of Shvo's catalyst monitored by real-time IR spectra. Black dot: 1-decene, red dot: *n*- and *i*-aldehyde, and blue dot: *n*- and *i*-alcohol. Decay of 1-decene until 50% conversion was fitted with first-order equation. Formation of *n*- and *i*-alcohol was fitted with zero-order reaction. Common conditions: DMA, 9 mL; H_2, 1.0 MPa; CO, 1.0 MPa. (a) 1-decene, 3 mmol; Shvo's cat, 125 μmol (based on mol of Ru atom). The rate constant was determined from the initial 50% conversion. (b) Undecanal, 3 mmol; Shvo's cat, 125 μmol (based on mol of Ru atom).

comparable results in product yields, reaction rates, and the substrate scope except that here formation of internal alkenes and formates as byproducts was observed in some cases.

Orthogonality. In our previous communication, we proposed that the orthogonality between Rh/XANTPHOS system and Shvo's hydrogenation catalyst was the key of our system. In order to prove it, we performed the following experiments. First, the reaction rates of both step of tandem hydroformylation/hydrogenation catalyzed by Rh/XANTPHOS/Shvo's system were compared with the separately performed each reaction under the same condition (in DMA, at 120 °C, under 2.0 MPa of H_2/CO). The compared reactions are summarized in Scheme 2: hydroformylation/hydrogenation of 1-decene by Rh/XANTPHOS/Shvo's cat. (reaction **a**), hydroformylation of 1-decene by Rh/XANTPHOS (reaction **b**), isomerization of 1-decene by Shvo's cat. (reaction **c**), and hydrogenation of undecanal by Shvo's cat. (reaction **d**). The experimental results are summarized in Figures 1 and 2.

The rate of hydroformylation of 1-decene by Rh/XANTPHOS system was not affected by the presence of Shvo's catalyst: The rate in the presence (reaction **a**, derived from Figure 1a) and in the absence (reaction **b** from Figure 1b) of Shvo's catalyst were both first order to the concentration of 1-decene until 95% conversion, and the observed rate constants were (6.4 ± 0.8) and $(6.6 \pm 0.8) \times 10^{-3}$ s^{-1}, respectively. In contrast, increases of *i*-alcohol and isomerized alkenes were observed in the presence of Shvo's catalyst (n/i = 16 and 24 in reactions **a** and **b**, respectively). The lower n/i in reaction **a** can be explained by the isomerization of 1-decene to internal alkenes mediated by Shvo's catalyst and successive hydroformylation of the internal alkenes by Rh/XANTPHOS.[16] When isomerization of 1-decene by Shvo's catalyst was independently performed, the reaction rate obeyed the first order kinetics on 1-decene concentration until 50% conversion,[17] and the rate constant was $(3.6 \pm 0.4) \times 10^{-4}$ s^{-1} (reaction **c**, derived from Figure 2a), which was 6% of the observed rate constant of hydroformylation of 1-decene by Rh/XANTPHOS (reaction **b**, Figure 2a). Slow hydrogenation of 1-decene to decane and hydroformylation of 1-decene to aldehyde was confirmed by the low yields of decane (3.9%) and alcohols (6.2%) in reaction **c**. When the rates of hydrogenation of undecanal by Shvo's catalyst in the presence and absence of Rh/XANTPHOS were compared (reactions **a** and **d**, Figures 1a and 2b), they were both zero order on the concentration of undecanal, and the observed reaction rates were (8.4 ± 0.8) and $(9.1 \pm 0.9) \times 10^{-5}$ mol/L·s, respectively. The decrease of the reaction rate was within the margin of error. Selectivity of aldehyde to alcohol was >95% in both cases.

In this context, we could conclude the presence of Shvo's catalyst did not affect the rate of hydroformylation by Rh/XANTPHOS but slightly decreased the selectivity. On the other hand, the presence of Rh/XANTPHOS might have decreased the rate of hydrogenation, but the difference is almost negligible.

Orthogonality was also demonstrated by comparing the above one-pot, one-step reaction with the one-pot, stepwise reaction shown in Scheme 3. First, hydroformylation of 1-decene was performed with Rh/XANTPHOS under H_2/CO. After the completion of the reaction, Shvo's catalyst was added to the mixture, and H_2/CO was purged by H_2. The yield and $n/$

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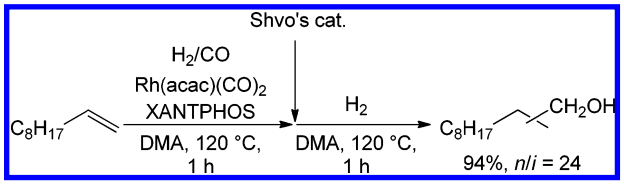
Scheme 3. Stepwise Hydroformylation/Hydrogenation



i of undecanol were about the same as the one-pot reaction (run 1 in Table 1), which indicates the presence of Shvo's catalyst did not affect the yield of hydroformylation by Rh/XANTPHOS at all. On the other hand, hydrogenation of undecanal under H_2 was much faster than under H_2/CO (<1 h versus ~10 h). As discussed above, the presence of Rh/XANTPHOS did not change the rate of hydrogenation by Shvo's catalyst. Therefore, poisoning of Shvo's catalyst by CO was confirmed.

Kinetics of Hydrogenation Catalyzed by Shvo's Catalyst under H_2/CO. The reaction rate of hydrogenation catalyzed by Shvo's catalyst under H_2/CO is very slow compared to under H_2.[18] Considering industrial application, it is a significant drawback to our catalyst system. Therefore, understanding the hydrogenation step in detail is important for further improvement of our system.

First, the effects of H_2 and CO pressure and Ru and XANTPHOS concentration on the reaction rate were determined by real time IR monitoring (Figure 3a–d). The varied parameters were CO and H_2 pressure (Figure 3a,b, respectively) and concentration of Shvo's cat and XANTPHOS (Figure 3c,d, respectively).

Based on the data obtained in Figures 2b and 3, the rate equation in the absence of XANTPHOS was expressed to be

$$-\mathrm{d}[\text{aldehyde}]/\mathrm{d}t = k_1[\text{aldehyde}]^0 P_{H_2} P_{CO}^{-1}[\text{Ru}] \quad (1)$$

In the presence of XANTPHOS, the rate of hydrogenation decreased. But the effect of XANTPHOS concentration could not be simply described. The rate eq 1 is different from the previously reported dependency on the concentration of

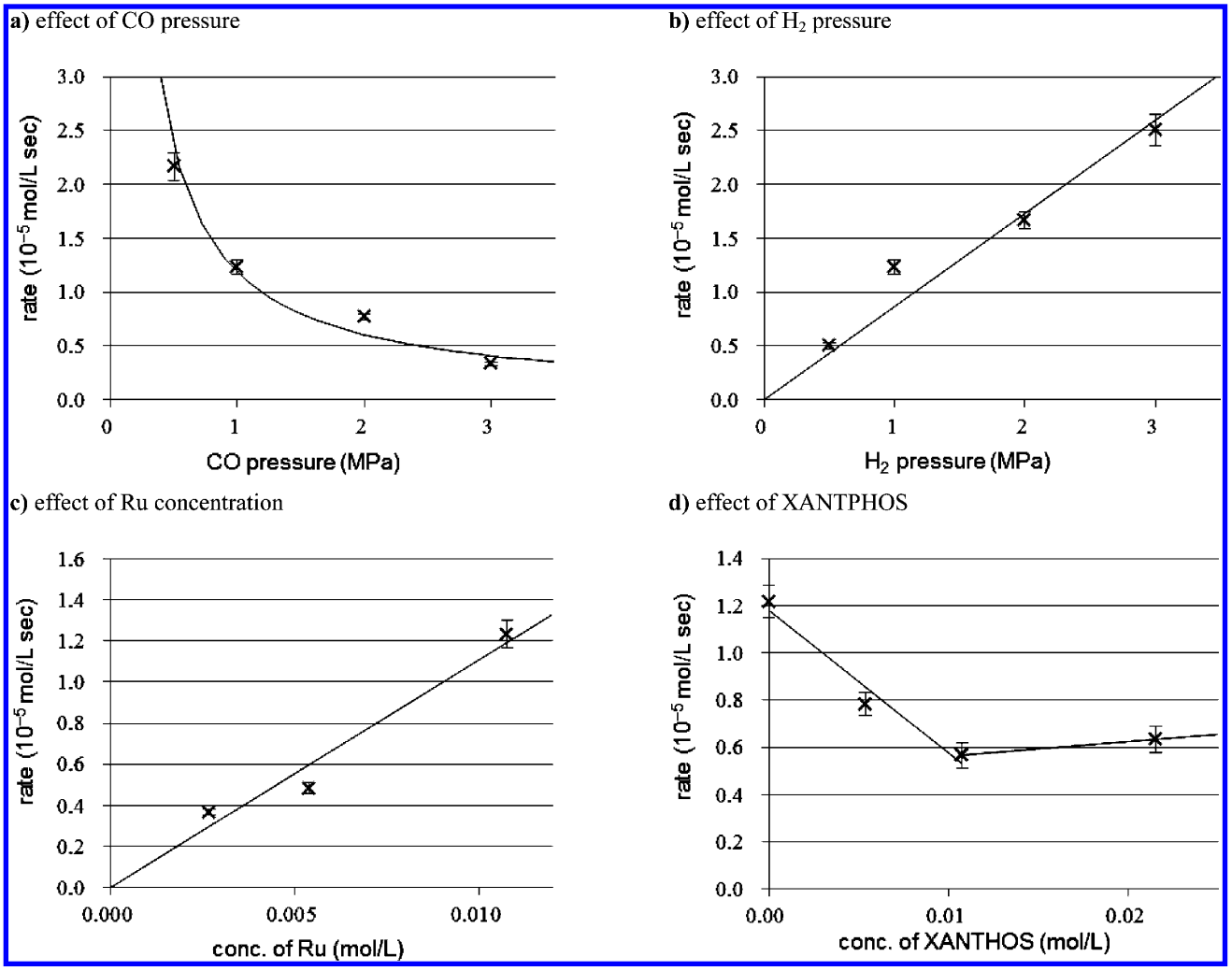


Figure 3. Rate of hydrogenation of undecanal catalyzed by Shvo's catalyst using H_2/CO under varying CO pressure (a), H_2 pressure (b), Ru concentration (c), and XANTPHOS concentration (d). Standard condition: DMA, 10 mL; H_2, 1.0 MPa; CO, 1.0 MPa; undecanal, 5 mmol; dodecane, 2.5 mmol (total 11.6 mL); Shvo's catalyst, 0.125 mmol (based on the mol of Ru atom). Selectivity from undecanal to undecanol is >95% in all cases. Rate constants were determined from time course of alcohols in initial 200 min by fitting with zero-order reaction. Obtained rate constants in each figure were fitted with inverse proportion to CO pressure in (a), direct proportion to H_2 pressure in (b), direct proportion to Ru concentration in (c), and direct proportion to XANTPHOS concentration in (d). In (d) two different lines are drawn for XANTPHOS concentration from 0 to 1.1×10^{-2} M and 1.1×10^{-2} to 2.2×10^{-2} M, respectively.

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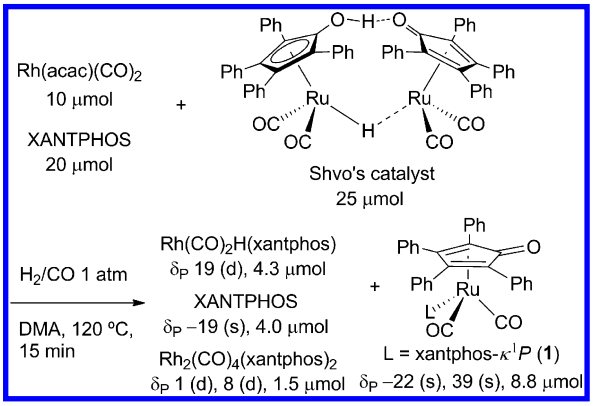
aldehyde in the hydrogenation of aldehyde by Shvo's catalyst under H_2.[13d−g] Accordingly, the change of reaction mechanism caused by poisoning of the catalyst by CO is suggested.[19]

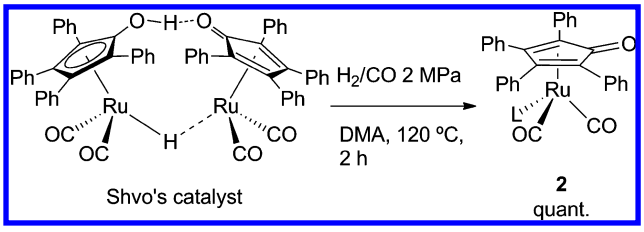
In the previous communication[12] we performed ^{31}P NMR spectroscopic analysis of the catalyst solution prepared by the treatment of $Rh(acac)(CO)_2$/XANTPHOS/Shvo's catalyst in DMA at 120 °C under 1.0 atm of H_2/CO for 15 min. Observed signals were assigned to be $Rh(CO)_2H$(xantphos) (δ_P 19 (d), 4.3 μmol), free XANTPHOS (δ_P −19 (s), 4.0 μmol), $Ru(CO)_2$(cyclopentadienone)(xantphos-κ^1P) (**1**) (δ_P −22 (s), 39 (s), 8.8 μmol), and $Rh_2(CO)_4$(xantphos)$_2$ (δ_P 1 (d), 8 (d), 1.5 μmol) (Scheme 4).[20] On the other hand, here we found

Scheme 4. Observed Species by ^{31}P NMR in Ref 12



that the Shvo's catalyst was quantitatively converted to $Ru(CO)_3$(cyclopentadienone) (**2**) by the treatment under higher H_2/CO pressure of 2.0 MPa (Scheme 5). Since the

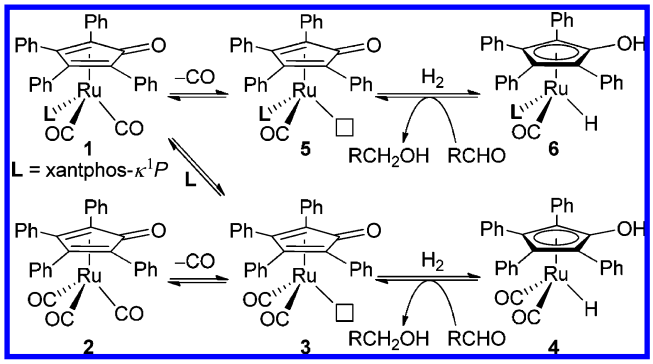
Scheme 5. Treatment of Shvo's Catalyst under H_2/CO Pressure



catalytic reaction employs high H_2/CO pressure, the major quantity of the Ru atoms most likely exists as **2**. From these observations, the reaction mechanism of hydrogenation under H_2/CO by Shvo's catalyst may be proposed as described in Scheme 6. Under high H_2/CO pressure, Ru species mainly exists as the tricarbonyl species **2**. Equilibrium to form a dimer[13g] was not involved in the rate-determining step considering that the rate equation is first order on Ru concentration. From **2**, dissociation of one CO molecule gives **3**, and successive metal−ligand cooperative activation of H_2 affording the Ru−H species **4** is the rate-determining step, which explains the fact that the reaction rate is first order on H_2 pressure and inverse first order on CO pressure. Once formed, **4** immediately reacts with aldehyde to give alcohol and return to **2** by rapid coordination of CO, resulting in zero-order contribution of the aldehyde concentration to the reaction rate.

In the presence of XANTPHOS, it coordinates to **3** to give **1**, which was detected by ^{31}P NMR experiment.[12] When Ru is coordinated by XANTPHOS (to form **1**), it becomes more

Scheme 6. Proposed Mechanism of Hydrogenation of Aldehyde



electron rich compared to **2** to strengthen the coordination of CO to Ru, thus it makes the formation of active species **6** from **1** via loss of CO to form **5** and successive metal−ligand cooperative activation of H_2 less favorable.[21] As XANTPHOS concentration was increased from 0 to 1 equiv to Ru, the reaction rate decreased because the ratio of XANTPHOS ligated Ru species was increased (Figure 3d, diagonal line).

In the presence of more than 1 equiv XANTPHOS to Ru, all the active species were XANTPHOS ligated Ru species, resulting in a constant reaction rate (Figure 3d, horizontal line) as a function of XANTPHOS concentration. In the presence of XANTPHOS, the reaction was gradually slowed down especially after 500 min.[22] It means there is a catalyst decomposition pathway caused by XANTPHOS. One explanation may be dissociation of cyclopentadienone by the steric repulsion with XANTPHOS. It should be noted however, the actual hydroformylation/hydrogenation was carried out with only a slight excess of XANTPHOS (the Rh/XANTPHOS/Ru ratio was 1/2/2.5 in the standard condition), and thus the deceleration of Ru-catalyzed hydrogenation by XANTPHOS should not have been problematic.

Comparison of Hydrogenation Activity of Ru Catalyst under H_2/CO. The hydrogenation activity of Shvo's catalyst was compared with other Ru complexes under H_2/CO. In the presence of CO, a very strong coordinating ligand to Ru, the hydrogenation rates were significantly decelerated in all of the examined Ru catalysts when compared to their originally reported rates under pure H_2 without CO. Interestingly, Shvo's catalyst is far more active than $Ru_3(CO)_{12}$, $Ru(CO)H_2(PPh_3)_3$, and Cp*Ru(cod)Cl/$Ph_2PCH_2CH_2NH_2$/^{t}BuOK[23] (Table 2 runs 1−4). Under H_2/CO, Shvo's catalyst exists as **2** (Scheme 5), and $Ru_3(CO)_{12}$ and $Ru(CO)H_2(PPh_3)_3$ are thought to be exist as $Ru_xH_yL_z$ (L = CO or PPh_3).[24] The rate of dissociation of CO might be comparable between them because IR absorption band of $\nu_{C\equiv O}$ for **2** (2081, 2026, 2005 cm^{-1}) and $Ru_4H_4(CO)_{12}$ (2081, 2067, 2030, 2024, 2008 cm^{-1}) is similar to each other (Scheme 7). Thus, the difference should be attributed to the rate difference in the subsequent steps: Shvo's catalyst hydrogenates aldehyde in outer sphere mechanism[13d−g] (Scheme 7, eq 2), while $Ru_3(CO)_{12}$ and $Ru(CO)H_2(PPh_3)_3$ hydrogenate aldehydes via coordination of aldehyde to Ru and insertion of the carbonyl group to Ru−H followed by hydrogenolysis (Scheme 7, eq 3). When Shvo's catalyst is compared to Cp*Ru(cod)Cl/$Ph_2PCH_2CH_2NH_2$/^{t}BuOK, electron density on Ru center might be the origin for the difference (Scheme 7, eqs 2 and 4). As discussed before, dissociation of one CO from **2** is necessary to generate hydrogenation active

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Table 2. Hydrogenation of Undecanal under H_2/CO with Various Catalysts[a]

run	cat	time (h)	conv (%)	alcohol (%)
1	Shvo's cat	11	99	99
2	$Ru_3(CO)_{12}$	12	<1	0
3	$Ru(CO)H_2(PPh_3)_3$	23	4.7	4.4
4[b]	$Cp^*Ru(cod)Cl/Ph_2PCH_2CH_2NH_2/^tBuOK$	12	21	<1[c]
5[d]	Shvo's cat	13	99	98
6[d]	$Cp^*Ru(cod)Cl/Ph_2PCH_2CH_2NH_2/^tBuOK$	10	85	16[c]

[a]Reaction conditions: DMA, 10 mL; H_2, 1.0 MPa; CO, 1.0 MPa; undecanal, 5 mmol; dodecane, 2.5 mmol; Ru complex, 0.125 mmol (based on the mol of Ru atom). [b]The mol ratio of $Cp^*Ru(cod)Cl:Ph_2PCH_2CH_2NH_2:{}^tBuOK$ = 1:1:1. [c]High-boiling products were observed by GC, which are considered to be dimers. [d]^{i}PrOH was used as solvent.

species **4** in the case of Shvo's catalyst. On the other hand, $Cp^*Ru(Ph_2PCH_2CH_2NH_2)H$ was reported to be the hydrogenation active species formed from $Cp^*Ru(cod)Cl/Ph_2PCH_2CH_2NH_2/{}^tBuOK$ under H_2.[23] After loss of dihydrogen, it forms coordinatively unsaturated 16e species, which would be trapped by CO to give $Cp^*Ru(CO)(Ph_2PCH_2CH_2NH)$. Regeneration of active species requires dissociation of CO from it. Since the Ru−CO bond is considered to be weaker in Shvo's system than Cp*RuPN system, (as reported values, IR absorption band of $\nu_{C\equiv O}$ = 2081, 2026, and 2005 cm^{-1} for **2** and 1904 cm^{-1} for $Cp^*Ru(CO)(NHPh)(P^iPrPh_2)$[25]), the regeneration of active species should be much easier to take place in Shvo's catalyst. When ^{i}PrOH, which was reported as the best solvent for $Cp^*Ru(cod)Cl/Ph_2PCH_2CH_2NH_2/{}^tBuOK$, was used for comparison, Shvo's catalyst was still more active and selective than Cp*RuPN system (runs 5 and 6).

Normal Selective Tandem Hydroformylation/Hydrogenation using Ru as a Single Component Catalyst. Rather to our surprise, the normal-selective tandem hydroformylation/hydrogenation of 1-decene did take place in the absence of Rh precursor; namely, a combination of Shvo's catalyst and XANTPHOS was active to mediate the tandem reaction, although the hydroformylation activity was lower compared to the dual catalyst.

The tandem hydroformylation/hydrogenation of 1-decene to *n*-alcohol was successfully accomplished when catalyzed by a combination of Shvo's catalyst or cyclopentadienone ligated Ru tricarbonyl complexes, and the results are summarized in Table 3. The examined cyclopentadienone Ru complexes were having phenanthrene-fused 2,5-diphenylcyclopentadienone (**7**),[26] 3,4-diphenyl-2,5-bis(ethoxycarbonyl)cyclopentadienone (**8**), and cyclopentane-fused 2,5- bis(trimethylsilyl)cyclopentadienone (**9**) (Figure 4). Since Shvo's catalyst was proven to have low activity for the hydroformylation of 1-decene in the above experiment, higher reaction temperature was employed for this investigation. When 1-decene was treated with a combination of Shvo's catalyst and XANTPHOS under H_2/CO at 160 °C, it gave *n*-alcohol in 47% yield as the major product with *n*/*i* of 32 (Table 3, run 1). It should be noted that the *n*/*i* value was even higher than Rh/XANTPHOS at 120 °C (*n*/*i* = 24 in Figure 1b). A major byproduct was isomerized alkenes (13%). The activity for hydroformylation was significantly affected by the cyclopentadinenone ligand (runs 2−4). A combination of **7**/XANTPHOS gave *n*-alcohol with similar yield and *n*/*i* to Shvo's catalyst. The activity and *n*/*i* were lower with **8**/XANTPHOS. The highest selectivity in the hydroformylation of 1-decene to *n*-undecanal was accomplished with **9**/XANTPHOS resulting in the highest yield of *n*-alcohol (73%, run 4). Although the reaction rates were quite low compared to Rh or Co, *n*/*i* selectivity is highest level among the reported tandem hydroformylation/hydrogenation catalysts.

Here we assume that (hydroxycyclopentadienyl)RuH(κ^2-XANTPHOS) (**C** in Figure 5) as the active species for both

Scheme 7. Comparison with Hydrogenation Mechanism with Various Ru Catalysts

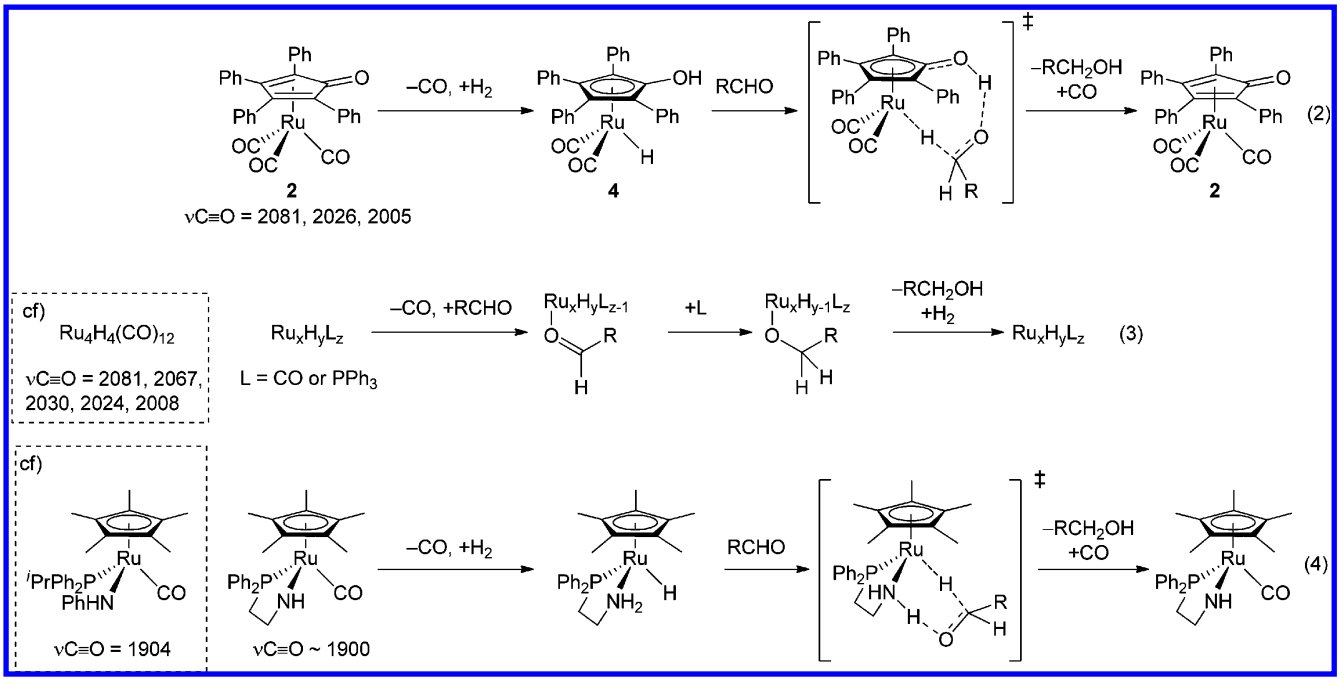

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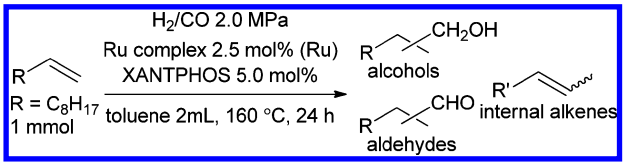
Table 3. Tandem hydroformylation/hydrogenation Catalyzed by Ru(CO)$_3$(cyclopentadienone) /XANTPHOS Systems[a]



run	cat.	conv. (%)	aldehydes (%)	*n*/*i*	alcohols (%)	*n*/*i*	internal alkenes (%)
1[b]	Shvo's cat/XANTPHOS	71	0.2	–	47	32	13
2	**7**/XANTPHOS	100	17	29	50	26	24
3	**8**/XANTPHOS	60	7.0	32	<1	–	50
4	**9**/XANTPHOS	98	1.2	–	73	29	12

[a]Reaction condition: 1-decene, 1.0 mmol; Ru complex, 25 μmol (based on Ru atom); XANTPHOS, 50 μmol; toluene, 2.0 mL; H_2, 1.0 MPa; CO, 1.0 MPa; 24 h. The yields in the table were determined by GC analysis with dodecane as internal standard, and *n*/*i* = (mol of *n*-product)/(mol of *i*-products). [b]XANTPHOS 25 μmol.

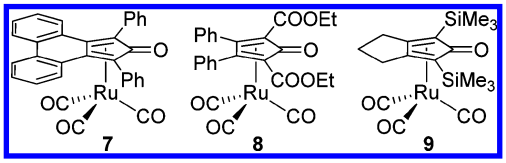


Figure 4. Investigated Ru(CO)$_3$(cyclopentadienone) complexes.

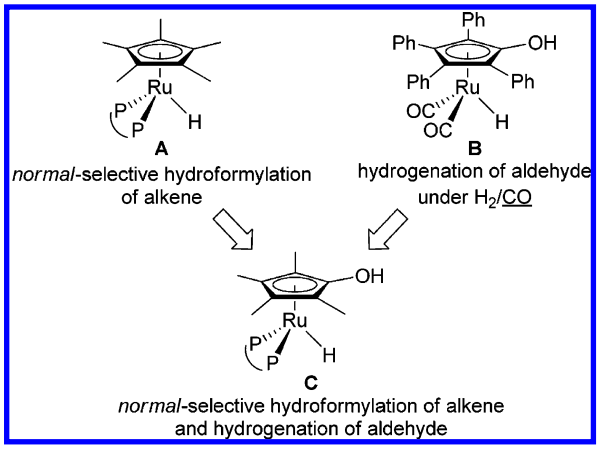


Figure 5. Conceptual explanation for Ru-based hydroformylation/hydrogenation catalyst and Ru catalyzed hydroformylation/hydrogenation.

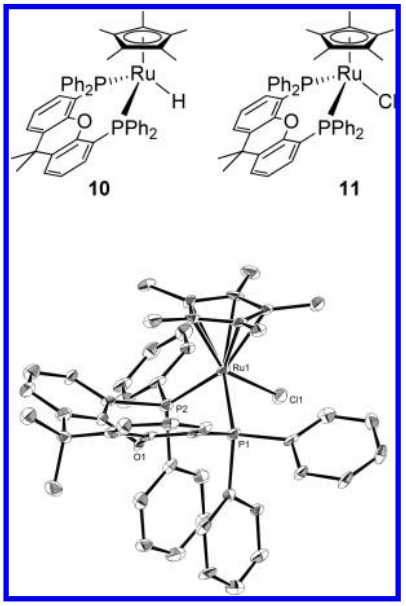


Figure 6. ORTEP drawing of Cp*Ru(xantphos)Cl (**11**). Thermal ellipsoids set at 50% probability; hydrogen atoms and solvent molecules are omitted for clarity.

hydroformlylation and hydrogenation. Recently, we reported the Ru-catalyzed normal-selective hydroformylation using (cyclopentadienyl)Ru/bisphosphine or bisphosphite systems.[26] In this paper, we isolated Cp*Ru(Xantphos)H[27] (**10**, corresponds to **A** in Figure 5) and confirmed that it worked as a catalyst precursor for hydroformylation of 1-decene with high *n*/*i* selectivity. The fact that the combination of Shvo's catalyst/XANTPHOS was active not only for hydrogenation of aldehyde but also for hydroformylation can be nicely explained by considering complex **C** as a bifunctional catalyst playing the roles of both **A** and **B** (Figure 5).

Although one might wonder if the bidentate coordination of XANTPHOS in a three-legged piano stool structure would cause a serious steric repulsion with the Cp* ligand, we isolated Cp*Ru(xantphos)Cl (**11**) and characterized it by X-ray single crystal analysis as shown in Figure 6.[27,28] Thus, for hydroformylation, either dissociation of one phosphorus atom or a partial dissociation of the cyclopentadienyl ligand in **C** would provide a vacant site for coordination−insertion of alkene and CO. For hydrogenation of aldehyde, either **B** or **C** should be responsible, although the details are still unknown.

CONCLUSION

In summary, we reported that our system could offer a new pathway to industrially important linear α,ω-diols from corresponding alkenyl alcohols or acetates. Other functional groups were also tolerate under our catalytic condition. The mutual orthogonality of Rh catalyzed hydroformylation and Ru catalyzed hydrogenation was proven by control experiments using real-time IR monitoring. Also, reaction mechanism of hydrogenation of aldehyde by Shvo's catalyst under H_2/CO pressure was investigated by real-time IR monitoring and ^{31}P NMR spectroscopy. Shvo's catalyst was found to be more active than the conventional Ru hydrogenation catalyst because of its robustness under CO pressure. Based on the above consideration, we propose the following three points for designing more active hydrogenation catalyst under H_2/CO pressure: (1) bifunctional type hydrogenation catalyst; (2) less electron-donating ligand on Ru; and (3) more basic functional group to activate H_2 on the ligand. Furthermore, here we found a Ru-based tandem *n*-selective hydroformylation/hydrogena-

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tion, which affords *n*-alcohol with low reaction rate but high *n*/*i* ratio. If a more active and recyclable catalyst is developed, these systems will be attractive alternative for industrial *oxo*-processes.

EXPERIMENTAL SECTION

General. All the manipulations involving the air- and moisture-sensitive compounds were carried out by using standard Schlenk technique or glovebox under argon purified by passing through a hot column packed with BASF catalyst R3-11. H_2/CO mixed gas (H_2:CO = 49.1:50.9) was purchased from Suzuki-Shoukan and used without further purification. Commercially available anhydrous *N*,*N*-dimethylacetamide, methanol, and 2-propanol were distilled and degassed by freeze−pump−thaw before use. Commercially available anhydrous toluene was passed through solvent purification column before use. 1-decene, dodecane, tridecane, allyl alcohol, allyl acetate, 3-butenyl alcohol, 3-butenyl acetate, and 4-pentenyl alcohol were purchased from TCI and distilled and degassed by freeze−pump−thaw before use. Undecanal styrene, vinylcyclohexane, 2-methyl-1-nonene, and (*Z*)-2-decene were purchased from TCI and degassed by freeze−pump−thaw before use. $Ru(CO)H_2(PPh_3)_3$ was purchased from TCI. Cp*Ru(cod)Cl was purchased from Strem. $Rh(acac)(CO)_2$ and $Ph_2PCH_2CH_2NH_2$ were purchased from Aldrich. Shvo's catalyst was prepared according to literature method from $Ru_3(CO)_{12}$ and tetraphenylcyclopentadienone and purified by recrystallization from toluene/hexane. 2-(5-hexen-1-yloxy)-tetrahydropyran,[28] (5-hexen-1-yloxy)methylbenzene,[29] (5-hexen-1-yloxy)-*tert*-butyldimethylsilane,[30] 2-(9-decen-1-yl)-1,3-dioxolan,[31] (5-hexen-1-yl)-*N*-phenylcarbamate,[32] XANTPHOS,[10] and **7**[33] were prepared by the literature method. Cp*Ru(xantphos)H (**10**) and Cp*Ru(xantphos)Cl (**11**) were prepared as a previously reported procedure by us.[26] Product yields were determined by Shimadzu GC-2014 equipped with InertCap 5MS/Sil capillary column (0.25 ID, 0.25 μm df, 30 m) using calibration curve made with dodecane or tridecane as an internal standard. Real-time IR measurement was performed by using Mettler Toledo ReactIR 45 and analyzed by icIR. NMR spectra were recorded on a JEOL JIN-ECP500 or JEOL-ECS400 spectrometers. Chemical shifts are reported in ppm relative to the residual protiated solvent for ^{1}H and external 85% H_3PO_4 for ^{31}P nuclei. Data are presented in the following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. NMR yields were determined by ^{1}H experiment with 15 s relaxation delay using 1,3,5-trimethoxybenzene as internal standard. IR spectra of solid sample were recorded by Shimadzu FTIR-8400. X-ray crystallographic analyses were performed on Rigaku Mercury CCD or Valimax Saturn diffractometer. Elemental analysis was performed by the Microanalytical Laboratory, Department of Chemistry, Graduate School of Science, the University of Tokyo.

General Procedure for Hydroformylation/Hydrogenation of Alkene. DMA (1.0 mL) was added to a stainless autoclave (50 mL) charged with $Rh(acac)(CO)_2$ (5.2 mg, 20 μmol), XANTPHOS (23.1 mg, 40.0 μmol), and magnetic stir bar under Ar, and the resulting mixture was stirred for 5 min at room temperature. Shvo's catalyst (27.1 mg, 50.0 μmol (Ru)) was weighed and dissolved in DMA (2.0 mL) under Ar, which was transferred to the autoclave by cannulation. A 2:1 mol ratio mixture of alkene (2.0 mmol) and internal standard (1.0 mmol) was added via syringe. The autoclave was pressurized with 2.0 MPa of H_2/CO and stirred at 120 °C, at 800 rpm for 12.5 h. When the autoclave was cooled with water/ice bath for 30 min, the pressure was released. 1,3,5-trimethoxybenzene (100 mg, 0.590 μmol) was added to the crude solution. Then the solution was analyzed by GC and ^{1}H NMR. NMR yield of *n*- or *i*-aldehydes was determined from the integration of corresponding formyl proton (δ 9.8, t, $-CH_2C\underline{H}O$, and δ 9.6, d, $-CHRC\underline{H}O$, respectively). NMR yield of *n*- or *i*-alcohols were determined from the alpha-proton of hydroxyl group (δ 3.6, t, $-CH_2C\underline{H_2}OH$, and δ 3.4−3.5, m, $-CHRC\underline{H_2}OH$). NMR yield of formats was determined by the integration of corresponding formyl proton (δ 8.0, s, $CH_2OC\underline{H}O$). The yields determined by ^{1}H NMR were consistent with those determined by GC.

Real-Time IR Monitoring of Hydroformylation/Hydrogenation of 1-Decene by $Rh(acac)(CO)_2$/XANTPHOS/Shvo's Catalyst. An autoclave (100 mL) equipped with IR probe, high-pressure dropping funnel and magnetic stir bar was charged with $Rh(acac)(CO)_2$ (13.0 mg, 50 mmol), XANTPHOS (57.8 mg, 100 mmol). After flushed with Ar, DMA (2 mL) was added via syringe to the autoclave. Shvo's catalyst (67.8 mg, 125 μmol (Ru)) was charged into 20 mL Shlenck under Ar and was dissolved in DMA (3.0 mL). Then the solution was transferred to the autoclave by cannulation, the Schlenk was washed two times with DMA (total 1.0 mL), and they were transferred to the autoclave. At the same time, the dropping funnel was charged with 1-decene (1.0 mL, ∼5.3 mmol) and DMA (3.0 mL). The autoclave was pressurized with 2.0 MPa of H_2/CO and stirred at 120 °C and 800 rpm for 1,5 h. Then the mixture of 1-decene and DMA in dropping funnel was pressed in to the autoclave with 3 MPa of H_2/CO, and the gas pressure was partially released to the value before substrate injection. The integration of the characteristic peaks for 1-decene (912 cm^{-1}, terminal C═C), undecanal (1726 cm^{-1}, C═O), and undecanol (1058 cm^{-1}, C−O) were monitored during the reaction time. After appropriate reaction time, the autoclave was cooled with water/ice bath for 30 min, and the pressure was released. Dodecane (500.0 mg, 2.945 mmol) was added to the crude solution. Then the solution was analyzed by GC.

The actual amount of substrate injected into the autoclave was estimated as sum of the observed product with GC analysis. The actual liquid volume was estimated with the following equation:

$$\begin{aligned}&(\text{actual liquid volume})\\&\quad=(\text{initial charge of solvent})+(\text{mixture of solvent and substrate charged via dropping funnel})\\&\quad=7+4\times(\text{mmol of the substrate injected into the autoclave})/(\text{mmol of the substrate charged into the dropping funnel})\end{aligned}$$

Data treatment of IR was as follows: Background was measured before experiment under air. During the reaction, the peak area for 1-decene (912 cm^{-1}, terminal C═C), undecanal (1726 cm^{-1}, C═O), and undecanol (1058 cm^{-1}, C−O) were plotted versus time (*t*) every 15 s (64 scans were integrated) for initial 1.5 h and every 5 min (256 scans were integrated) after that time. Signal to noise ratio of these peaks of compounds at concentration of 0.32 M in DMA was ∼40, 60, and 70 respectively, which supports the accuracy of the integral value. The consumption of 1-decene until 95% conversion was monitored to confirm the first-order kinetics. The obtained pseudofirst-order rate constant was multiplied by the selectivity to aldehyde to calculate rate constant for hydroformylation. Since the increase of 1-undecanol was linear versus time, the observed rate constant was calculated from the slope.

As experimental error, the amount of injected substrate ±5%, H_2/CO pressure ±2.5%, volume of liquid ±1.0%, the amount of weighed catalyst <0.8%, was considered (±9.6% in total). Statistical error was respectively determined as standard deviation from obtained data and its least-squares fitting curve. The total error (%) was calculated as multiple of experimental and statistical error.

Real-Time IR Monitoring of Hydroformylation of 1-Decene by $Rh(acac)(CO)_2$/XANTPHOS. An autoclave (100 mL) equipped with IR probe and high pressure dropping funnel was charged with $Rh(acac)(CO)_2$ (13.0 mg, 50 μmol) and XANTPHOS (57.8 mg, 100 μmol), and magnetic stir bar was flushed with Ar. The IR monitoring was started at this point. DMA (7.0 mL) was added, and the resulting mixture was stirred for 5 min at room temperature. At the same time, the dropping funnel was charged with 1-decene (1.0 mL, 5.3 mmol) and DMA (3.0 mL). The autoclave was pressurized with 2.0 MPa of H_2/CO and stirred at 120 °C and 800 rpm for 1.5 h. Then the mixture of 1-decene and DMA in dropping funnel was pressed into the autoclave with 3 MPa of H_2/CO, and the gas pressure was partially released to the value before substrate injection. The concentration of

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1-decene and undecanal was monitored by the integration of the area at 1-decene (912 cm^{-1}, terminal C═C) and undecanal (1726 cm^{-1}, C═O) . After appropriate reaction time, the autoclave was cooled with water/ice bath for 30 min, and the pressure was released. Dodecane (500.0 mg, 2.945 mmol) was added to the crude solution. Then the solution was analyzed by GC. Following data treatments were similar to that mentioned above.

Real-Time IR Monitoring of Isomerization of 1-Decene by Shvo's Catalyst. Shvo's catalyst (67.8 mg, 125 μmol) was charged into 20 mL Shlenck under Ar and dissolved in DMA (5.0 mL). An autoclave (100 mL) equipped with IR probe and magnetic stir bar was flushed with Ar. IR monitoring was started at this point. Then the solution of Shvo's catalyst was added to the autoclave by cannulation, the Schlenk was washed two times with DMA (total 5.0 mL), and they were transferred to the autoclave. At the same time, the dropping funnel was charged with 1-decene (1.0 mL, c.a. 5.3 mmol) and DMA (3.0 mL). The autoclave was pressurized with 2.0 MPa of H_2/CO and stirred at 120 °C and 800 rpm for 1.5 h. Then the mixture of 1-decene and DMA in dropping funnel was pressed in to the autoclave with 3 MPa of H_2/CO, and the gas pressure was partially released to the value before substrate injection. The integration of the characteristic peaks for 1-decene (912 cm^{-1}, terminal C═C) was monitored during the reaction time. After appropriate reaction time, the autoclave was cooled with water/ice bath for 30 min, and the pressure was released. Dodecane (500.0 mg, 2.945 mmol) was added to the crude solution. Then the solution was analyzed by GC. Initially the reaction rate was first order on substrate concentration. The rate constant for the consumption of 1-decene until 50% conversion was calculated from the plot of $\ln(1 - [\text{1-decene}]/[\text{1-decene}]_0)$ versus time. The rate constant for isomerization was calculated as (rate constant for the consumption of1-decene) × (selectivity to internal alkenes)

Real-Time IR Monitoring of Hydrogenation of Undecanal by Shvo's Catalyst. Shvo's catalyst (67.8 mg, 125 μmol) was charged into 20 mL Shlenck under Ar and dissolved in DMA (5.0 mL). An autoclave (100 mL) equipped with IR probe and magnetic stir bar was flushed with Ar. IR monitoring was started at this point. Then the solution of Shvo's catalyst was added to the autoclave by cannulation, the Schlenk was washed two times with DMA (total 5 mL), and they were transferred to the autoclave. At the same time, the dropping funnel was charged with undecanal (1.1 mL, c.a. 5.3 mmol) and DMA (3.0 mL). The autoclave was pressurized with 2.0 MPa of H_2/CO and stirred at 120 °C and 800 rpm for 1.5 h. Then the mixture of 1-decene and DMA in dropping funnel was pressed in to the autoclave with 3 MPa of H_2/CO, and the gas pressure was partially released to the value before substrate injection. The integration of the characteristic peaks for undecanal (1726 cm^{-1}, C═O), and undecanol (1058 cm^{-1}, C−O) was monitored during the reaction time. After appropriate reaction time, the autoclave was cooled with water/ice bath for 30 min, and the pressure was released. Dodecane (500.0 mg, 2.945 mmol) was added to the crude solution, and then the solution was analyzed by GC. Following data treatments were similar to that mentioned above.

Stepwise Hydroformylation/Hydrogenation of 1-Decene. DMA (2.0 mL) was added to a stainless autoclave (50 mL) charged with $Rh(acac)(CO)_2$ (5.2 mg, 20 μmol), XANTPHOS (23.1 mg, 40.0 μmol), and magnetic stir bar under Ar, and the resulting mixture was stirred for 5 min at room temperature. A 2:1 mol ratio mixture of 1-decene (2.0 mmol) and dodecane (1.0 mmol) was added via syringe. The autoclave was pressurized with 2.0 MPa of H_2/CO and stirred at 120 °C and 800 rpm for 1 h. Then the autoclave was cooled with water/ice bath for 10 min, and the pressure was released. Shvo's catalyst (27.1 mg, 50.0 μmol (Ru)) was weighed and dissolved in DMA (2.0 mL) under Ar, which was transferred to the autoclave by cannulation. The autoclave was pressurized with 1.0 MPa of H_2 and stirred at 120 °C and 800 rpm for 1 h. Then the autoclave was cooled with water/ice bath for 30 min, the pressure was released, and the solution was analyzed by GC. Obtained products were *n*-alcohol 90%, *i*-alcohol 3.6%, *n*-aldehyde 1.9%, *i*-alcehyde 0.5%, decane 1.0%, undecyl formate 0.6%.

Real-Time IR Monitoring of Hydrogenation of Undecanal by Various Ru Catalysts under Various Conditions. Appropriate amount of Ru catalyst (125, 62.5, or 31.3 μmol) was charged into 20 mL Shlenck under Ar and dissolved in solvent (5.0 mL). An autoclave (100 mL) equipped with IR probe and magnetic stir bar was charged with appropriate amount of XANTPHOS (0, 62.5, 125, or 250 μmol) and flushed with Ar. IR monitoring was started at this point. Then the solution of Shvo's catalyst was added to the autoclave by cannulation, the Schlenk was washed two times with solvent (total 5.0 mL), and they were transferred to the autoclave. A mixture of undecanal and dodecane (2:1 mol ratio, 1.6 mL, 5.0 and 2.5 mmol) was introduced into the autoclave via syringe and was immediately pressurized with 2.0 MPa of H_2/CO and stirred at 120 °C and 800 rpm. The integration of the characteristic peaks for undecanol (1058 cm^{-1}, C−O) was monitored during the reaction time. After appropriate reaction time, the autoclave was cooled with water/ice bath for 30 min, and the pressure was released. Dodecane (500.0 mg, 2.945 mmol) was added to the crude solution. Then the solution was analyzed by GC. Following data treatments were similar to that mentioned above except that the rate constants were determined from the time course of alcohol in initial 200 min.

As experimental errors, the amount of injected substrate ±1.0%, H_2/CO pressure ±2.5%, volume of liquid ±1.0%, the amount of weighed catalyst <0.8% were considered (±5.4% in total). Statistical error was respectively determined as standard deviation from obtained data and its least-squares fitting curve.

Treatment of Shvo's Catalyst under H_2/CO. Shvo's catalyst (50 mg, 92 μmol) was charged into autoclave under Ar and dissolved in toluene (2.0 mL). The autoclave was pressurized with 2.0 MPa of H_2/CO and stirred at 120 °C for 2 h. After cooled to room temperature, the pressure was released, and the solution was transferred to glass vial in groove box. Evaporation of the solvent yielded slightly yellowish powder, which was confirmed to be almost pure $Ru(CO)_3$(2,3,4,5-tetraphenylcyclopentadienone) by ^{1}H NMR and IR spectroscopy.

Hydroformylation/Hydrogenation of 1-Decene by Ru Singular Catalyst. To a stainless autoclave (50 mL) charged with Ru complex (25.0 μmol), XANTPHOS (28.9 mg, 50.0 μmol) and magnetic stir bar under Ar, toluene (2.0 mL) and 2:1 mol ratio mixture of 1-decene and dodecane (total 300 μL, 1-decene 1.0 mmol, dodecane 0.5 mmol) were added via syringe. The autoclave was pressurized with 2.0 MPa of H_2/CO and stirred at 160 °C and 800 rpm for 24 h. Then the autoclave was cooled with water/ice bath for 30 min, and the pressure was released. Then the solution was analyzed by GC.

Preparation of Tricarbonyl(2,5-bis(ethoxycarbonyl)3,4-diphenylcycopentadienone)ruthenium (8). To a 50 mL double-necked round-bottomed flask containing $Ru_3(CO)_{12}$ (506.9 mg, 2.379 mmol(mol Ru)) and 2,5-bis(methoxycarbonyl)3,4-diphenylcyclopentadienone (878.9 mg, 2.335 mmol), toluene 17 mL was added and refluxed until starting materials were consumed as confirmed by TLC. After cooled, the reaction mixture to room temperature, and the solvent was evaporated. Desired product was recrystallized from $CHCl_3$/hexane to give yellow crystals (766.3 mg, yield 58.5%). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 0.97 (t, J = 7 Hz, 6H) 4.03 (dq, J = 16, 7 Hz, 2H), 4.05 (dq, J = 16, 7 Hz, 2H), 7.21−7.33 (m, 10H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 13.4 (CH_3), 61.3 (CH_2), 70.8 (4°), 109.5 (4°), 128.0 (CH), 129.1 (CH), 131.1 (CH), 164.7 (4°), 170.8 (4°), 192.1 (4°); mp 165−169 °C (decomp.); IR (KBr, cm^{-1}):1653 (s), 1709 (s), 1722 (s), 2002 (s), 2029 (s), 2100 (s). Anal. calcd for $C_{26}H_{20}O_8Ru$: C, 55.61; H, 3.59. Found: C, 55.38; H, 3.61.

Preparation of Tricarbonyl(2,4-bis(trimethylsilyl)bicycle-[3,3,0]octa-1,4-dien-3-one)ruthenium (9). To a 50 mL stainless autoclave, 1,7-bis(trimethylsilyl)-hepta-1,6-diyne (970 μL, 3.3 mmol) and trirutheniumdodecacarbonyl (700 mg, 1.095 mmol) are charged with acetonitrile 50 mL. Then the autoclave was pressurized with CO 0.5 MPa, and the resulting mixture was stirred at 120 °C for 12 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and passed through a short silica gel column. The volatiles of the filtrate were evaporated, and then the residue was recrystallized from toluene at −35 °C (1.011 g, yield 68.0%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.26 (s, 18H) 1.75−1.89 (m, 1H), 2.33 (m, 1H), 2.50−2.67 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 0.07 (CH_3), 25.8 (CH_2), 70.8 (4°), 109.5

(4°), 128.0 (CH), 129.1 (CH), 131.1 (CH), 164.7 (4°), 170.8 (4°), 192.1 (4°); mp;146−147 °C (decomp.), IR (KBr, cm^{-1}):1609, 2006, 2070. Anal. calcd for $C_{17}H_{24}O_4RuSi_2$: C, 45.41; H, 5.38. Found: C, 45.25; H, 5.34.

Recrystallization of 11. Rutheniumu complex **11** was synthesized according to our previous report.[26] The solid material was dissolved in THF, and hexane was allowed to slowly difusse into the solution to give single crystals suitable for X-ray analysis.

■ ASSOCIATED CONTENT

Supporting Information

Figures of plot of $\ln(1 - [1\text{-decene}]/[1\text{-decene}]_0)$ versus time for hydroformylation/hydrogenation, hydroformylation, and isomerization of 1-decene, time course of formation of undecanol by hydrogenation of undecanal by Shvo's catalyst under various conditions, and details for **8**−**11** by X-ray crystallographic analysis. 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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(16) Hydroformylation of internal alkene by Rh/XANTPHOS can produce *n*-aldehyde via isomerization to terminal alkene and successive *n*-selective hydroformylation. However the *n*/*i* was as low as 1.

(17) The consumption of 1-decene gradually got slower than first order.

(18) For example in the ref 13f, hydrogenation of benzaldehyde (0.97 M) by Shvo's catalyst (2.4−5.2 mM) under H_2 (3.5 MPa) at 60 °C gave the reaction rate of $-d[\text{benzaldehyde}]/dt = -3.5 \times 10^{-4}$ (mol/L·s), which is 10 times faster than our case ($-d[\text{undecanal}]/dt = -1.1 \times 10^{-5}$ (mol/L·s), with undecanal 0.43 M, Shvo's cat 11 mM, H_2 1.0 MPa, CO 1.0 MPa at 120 °C). Considering the difference of temperature (65 °C versus 120 °C), the reaction rate should 100−1000 times slower in the presesnce of CO.

(19) Casey et al. reported negative effect of the presence of PPh_3 on the rate of hydrogenation of aldehyde at relatively high temperature (>60 °C), but the rate was still first order on aldehyde concentration (ref 13f). Therefore, the change of the rate equation in our experiment ascribed to the presence of CO.

(20) The stoichiometry of the observed species does not represent the actual stoichiometry under catalytic condition, which employs higher H_2/CO pressure (2.0 MPa compared to 0.1 MPa in NMR experiment.)

(21) As a similar example to **1**, $\nu_{C\equiv O}$ for Ru(tetraphenylcyclopentadienone)$(CO)_2(PPh_3)$ was reported. (2037, 2011, 1981, 1955 cm^{-1}). The lower $\nu_{C\equiv O}$ for this compound than **2** (2081, 2026, 2005 cm^{-1}) indicates the cooridination of triaryl phosphine makes Ru−CO bond stronger. For Ru(tetraphenylcyclopentadienone)$(CO)_2(PPh_3)$, see:

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(28) Casey et al. isolated Ru(tetraarylcyclopentadienone)$(PPh_3)_2(CO)$ (with X-ray single crystal analysis), which supports the possibility of coordination of two triaryl phosphine ligand to Ru in spite of steric repulsion with tetraarylcyclopentadienone: Casey, C. P.; Stroman, N. A.; Beetner, S. E.; Johnson, J. B.; Priebe, D. C.; Guzei, I. A. *Organometallics* **2006**, *25*, 1236.
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