

High-Pressure IR Studies on the Asymmetric Hydroformylation of Styrene Catalyzed by Rh(I)-(R,S)-BINAPHOS

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Rhodium-catalyzed asymmetric hydroformylation of styrene using (*R,S*)-BINAPHOS (**1a**) and its methoxy-substituted derivative **1b** as chiral ligands was monitored by in situ high-pressure IR. The rate of aldehyde production is given by $r_{\text{obs}} = k_{\text{obs}}[\text{Rh}]^{1.0}[\text{styrene}]^{0.6}[\mathbf{1b}]^{-0.1}P_{\text{CO}}^{-0.9}$ (k_{obs} is a constant under isothermal conditions). The higher catalytic activity of the Rh-**1b** catalyst compared with that of Rh-**1a** is attributed to a higher concentration of the active species, which is generated by dissociation of CO from the major resting state RhH(CO)₂(**1**) (**2**). A rhodium carbonyl species **10**, the structure of which is unknown, is suggested to be formed from the rhodium hydride RhH(CO)₂(**1**) (**2**), especially when the rhodium concentration is high. Complex **10** is less active for hydroformylation and is probably responsible for the loss of %ee observed at high rhodium concentrations.

Introduction

Optically active aldehydes are versatile intermediates for the synthesis of many biologically active compounds, and asymmetric hydroformylation of olefins is one of the most straightforward synthetic strategies for such compounds.¹ Previously, we reported that the phosphine-phosphite (*R,S*)-BINAPHOS (**1a**) is an efficient chiral modified ligand for rhodium-catalyzed asymmetric hydroformylation of various olefins.² Recently, we reported that substitution at the 3-position of the phenyls in the phosphine part of **1a** with a methoxy (**1b**) or an isopropoxy (**1c**) group raised the regio- and enantioselectivities in the hydroformylation of aryl-ethenes and aliphatic alkenes.³ We thus became interested in how the substituents at the 3-position improved the catalytic activity and initiated a high-pressure infrared spectroscopic kinetic study of BINAPHOS/Rh-catalyzed asymmetric hydroformylation.

High-pressure IR and NMR have been recognized as powerful means to elucidate the intermediate complexes under hydroformylation conditions, for both unmodified Rh-catalysts^{4,5} and phosphine-modified Rh-catalysts.^{6–9} Thus, Garland reported kinetic studies on the unmodi-

fied system that showed that hydrogenolysis is the rate-determining step in that system for styrene hydroformylation;⁴ in situ IR spectroscopy revealed that an acylrhodium complex, Rh(acyl)(CO)₄, was the resting state of the catalyst.^{4,5,10,11} On the other hand, Bergounhou reported that the hydroformylation of styrene catalyzed by Rh/1,2,5-triphenyl-1*H*-phosphole is first order in both styrene concentration and hydrogen pressure.¹² Van Leeuwen has reported that, using a rhodium complex of a monodentate bulky phosphite, the rate-determining step varies depending on the olefins employed, viz., hydrogenolysis for 1-octene and olefin coordination for cyclohexene,¹³ whereas the styrene coordination step is a candidate for the rate-determining step when the hydroformylation is carried out at high pressure with the bidentate ligand BDPP.¹⁴ Van Leeuwen has also reported several steps may contribute to the reaction rate in 1-octene hydroformylation catalyzed by Rh and a monodentate phosphorus diamide as a ligand.⁸ Thus, even with the same catalyst system, the rate-determining step can vary depending on the substrates or reaction conditions.¹⁵ Previously, we reported mecha-

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Table 1. Asymmetric Hydroformylation of Olefins Catalyzed by Rh(acac)(CO)₂/1 (1:4)^a

run	olefin	ligand	P _{H₂} /P _{CO} (atm)	temp (°C)	time (h)	conv (%)	isoselect. (%)	%ee of iso-
1	styrene ^b	1a	10/10	60	20	>99	88.0	93.2 (<i>R</i>) ^j
2		1a	50/50	60	43	>99	88	94 (<i>R</i>) ^j
3		1a	10/10	23	22	21	90.6	95.2 (<i>R</i>) ^j
4		1b	10/10	60	20	>99	92.5	95.0 (<i>R</i>) ^j
5		1b	10/10	23	22	34	95.0	97.5 (<i>R</i>) ^j
6		1c	10/10	60	20	>99	91.1	95.7 (<i>R</i>) ^j
7		1c	10/10	23	22	25	94.0	98.3 (<i>R</i>) ^j
8	2-vinylnaphthalene ^c	1a	10/10	60	4	>99	83.4	81.9 (<i>R</i>)
9		1b	10/10	60	4	>99	89.4	82.3 (<i>R</i>)
10		1c	10/10	60	4	>99	87.8	93.2 (<i>R</i>)
11	1-hexene ^b	1a	10/10	30	40	34	24.3	80.2 (<i>R</i>) ^j
12		1b	10/10	30	40	66	29.8	90.0 (<i>R</i>) ^j
13	vinyl acetate ^c	1a	10/10	60	15	68	87.2	86.1 (<i>S</i>)
14	<i>d</i>	1a	50/50	60	36	>99	86	92 (<i>S</i>) ⁱ
15	<i>c</i>	1b	10/10	60	15	96	93.7	86.6 (<i>S</i>)
16	<i>c</i>	1c	10/10	60	15	92	83.7	90.2 (<i>S</i>)
17	indene ^e	1a	10/10	60	20	34	89.6	83.3 (<i>R</i>) ^j
18		1b	10/10	60	20	49	91.3	88.9 (<i>R</i>) ^j
19	(<i>Z</i>)-2-butene	1a	16/16	60	8	(23) ^g		82.0 (<i>R</i>) ^j
20		1b	16/16	60	9	(7.6) ^g		89.9 (<i>R</i>) ^j
21	methyl <i>N</i> -acetamidoacrylate	1a ^f	10/10	80	40	57	>99 ^h	54.6 (<i>R</i>)
22		1c ^f	10/10	80	40	83	>99 ^h	56.5 (<i>R</i>)

^a A solution of styrene (1.04 g, 10.0 mmol), Rh(acac)(CO)₂ (1.3 mg, 5.0 μmol), and **1** (15.4 mg, 0.020 mmol) in benzene (0.5 mL) was treated with carbon monoxide and hydrogen. ^b Substrate/catalyst = 2000 ([Rh] = 3.0 mM). ^c Substrate/catalyst = 1000 ([Rh] = 5.0 mM for 2-vinylnaphthalene, 7.0 mM for vinyl acetate). ^d Substrate/catalyst = 400. ^e Substrate/catalyst = 250 ([Rh] = 7.7 mM). ^f RhH(CO)(PPh₃)₃ was used as a precursor instead of Rh(acac)(CO)₂. Substrate/catalyst = 50 ([Rh] = 6.7 mM). ^g Turnover frequency ([Rh] = 0.83 mM). ^h Hydrogenation was observed as a side reaction. Hydroformylation product/hydrogenation product = 90:10 (run 21) and 92:8 (run 22). ⁱ Data taken from ref 2a. ^j Reported in our preliminary communication, ref 3.

nistic studies on hydroformylation catalyzed by Rh-(*R,S*)-BINAPHOS, in which the following two features were disclosed: (1) the olefin insertion into the rhodium-hydride bond is irreversible, and (2) the reaction rate is independent of hydrogen pressure.¹⁶ In this paper, with the aid of high-pressure IR, we further elucidate mechanistic aspects of the reaction, especially the formation and decomposition of the active species.

Results and Discussions

Hydroformylation of Various Olefins with Rh Complexes of MeO- or *i*-PrO-Substituted BINAPHOS. Asymmetric hydroformylation of styrene, 2-vinylnaphthalene, 1-hexene, vinyl acetate, indene, (*Z*)-2-butene, and methyl *N*-acetamidoacrylate was examined using Rh(acac) complexes of BINAPHOS (**1a**), 3-MeO-BINAPHOS (**1b**), and 3-*i*-PrO-BINAPHOS (**1c**) as catalyst precursors. The results are summarized in Table 1. For all of the olefins, the isoselectivity and the %ee values were higher using **1b** and **1c** compared to those obtained using **1a**.

Catalyst Precursors and Induction Period. Hydroformylation of styrene was carried out under H₂ (5 atm) and CO (5 atm) at 60 °C, and the reaction was followed by the decay of the IR absorption at 911 cm⁻¹ (alkene C-H of styrene, out-of-plane deformation vibration) and by the appearance of the aldehyde, C=O stretching vibration at 1727 cm⁻¹ (Figure 1, plot a). An induction period of ca. 20 min was observed. This agrees with the previous studies that incubation of the catalyst under a H₂/CO atmosphere is necessary in order to form the key intermediate RhH(CO)₂(ligand).⁸ We next examined the hydroformylation reaction using preformed

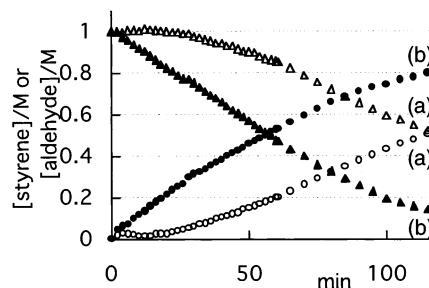


Figure 1. Concentrations of styrene and aldehydes with Rh(acac)(**1b**) and RhH(CO)₂(**2b**). Conditions: [styrene]₀ (initial concentration of styrene) = 1.0 M, [Rh] = 1.0 mM, [**1b**] = 4.0 mM, P_{H₂} = P_{CO} = 5 atm (constant), 60 °C. With Rh(acac)(**1b**): ○ aldehyde, △ styrene (plot a). With RhH(CO)₂(**2b**) prepared from Rh(acac)(**1b**) and H₂/CO at 60 °C for 2 h: ● aldehyde and ▲ styrene (plot b).

RhH(CO)₂(**2b**). After treatment of Rh(acac)(**1b**) with H₂ (5 atm) and CO (5 atm) at 60 °C for 2 h, the pressure was released, styrene introduced, and the mixture repressurized with H₂ (5 atm) and CO (5 atm). The decrease of the IR absorption of styrene and the increase of the aldehyde absorptions started immediately after the reintroduction of H₂/CO (Figure 1, plot b).

The formation of the rhodium hydride **2** from Rh(acac)(**1a**) was confirmed by IR as follows. When a Rh(acac)(**1a**) solution in benzene (50 mM) was treated with H₂ (20 atm) and CO (20 atm) at 40 °C, we observed the formation of three peaks at 2049, 2014, and 1969 cm⁻¹. The wavenumbers of these peaks are identical with those of RhH(CO)₂(**1a**) (**2a**) recently reported by van Leeuwen.¹⁷ Similarly, the formation of **2b** from Rh(acac)(**1b**) was confirmed by the appearance of absorption peaks at 2043 (Rh-H), 2013 (Rh-CO), and 1968 (Rh-CO) cm⁻¹ (Figure 2). Under conditions of H₂ (20

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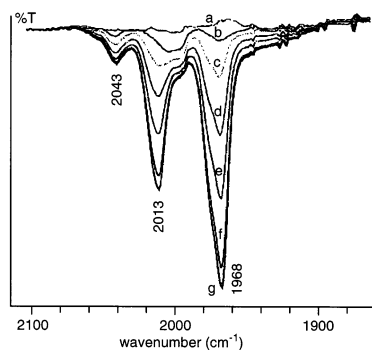


Figure 2. HP IR spectra for the preparation of **2b** from Rh(acac)(**1b**). Conditions: [Rh(acac)(**1b**)] = 50 mM, [free **1b**] = 50 mM, P_{H_2} = 20 atm, P_{CO} = 20 atm, 40 °C. (a) Rh(acac)(**1b**) without H₂/CO; (b) 0 min with H₂/CO; (c) 12 min; (d) 24 min; (e) 36 min; (f) 48 min; (g) 60–96 min (constant).

atm), CO (20 atm), 40 °C, HPIR revealed that 1 h was required before the concentration of RhH(CO)₂(**1b**) (**2b**) reached a constant value; at lower pressures of H₂ (10 atm) and CO (10 atm), 4.6 h was required. The peak at around 2000 cm⁻¹ has not yet been characterized.

It should be noted that the H₂/CO pressure during the incubation period significantly affects the %ee of the isoaldehyde, Table 2. Without incubation, hydroformylation under a total pressure of 20 atm (H₂/CO = 1:1) afforded the isoaldehyde with 94.9% ee (run 1). Exposure to air does not significantly affect the selectivity (run 2). Similarly, catalysts prepared by incubation of Rh(acac)(**1b**) at 40 °C under a total pressure of 20 atm for 2 h to form the hydride **2b** gave selectivities that are not affected by the conditions of styrene introduction (compare runs 1 and 2 with runs 3 and 4). On the other hand, when **2b** was prepared under a total pressure of 70 atm for 2 h, followed by pressure release to 1 atm prior to styrene introduction, resulted in a significant loss of %ee, 82.5% (run 5). This drop in %ee can be avoided by shortening the incubation time to 0.5 h (run 6), by the introduction of styrene without pressure release (runs 7 and 8), or by performing the hydroformylation under higher pressure, 70 atm (run 9).

Improved Reaction Rate with 3-MeO-BINAPHOS (1b) and 3-*i*-PrO-BINAPHOS (1c) Complexes. The reaction rates using **2b** and RhH(CO)₂(**1c**) (**2c**) have been compared with that obtained using **2a** as a catalyst. Before styrene introduction, Rh(acac)(**1**) was converted into RhH(CO)₂(**1**) (**2**) and the resulting **2** used in the hydroformylation reaction under the conditions of run 6 in Table 2. The reactions were monitored by IR, and the increase in aldehyde concentration was plotted against time (Figure 3). The initial rates, expressed as increase of aldehyde concentration per second, were calculated over the region of conversion 0–40% and found to be $r_{obs} = 6.3 \times 10^{-5}$ (**2a**), 14.9×10^{-5} (**2b**), and 14.7×10^{-5} M·s⁻¹ (**2c**). The observed aldehyde production rate (= styrene decay rate) r_{obs} using **2b** and **2c** is about twice that using **2a**. Thus, substitution at the 3-position of phenyls in BINAPHOS improves not only the selectivity but also the catalytic activity.

Kinetic Studies with 2b. For the reaction with **2b**, the effect of the concentration of each component on the

aldehyde production rate r_{obs} has been studied, and the results are summarized in Table 3. The hydrogen partial pressure does not influence the rate (runs 1 and 2, see also ref 16), while higher carbon monoxide partial pressures retard the reaction (runs 1 and 3–6). The reaction rate is calculated to be -0.9 order in CO pressure. Higher concentrations of the ligand also slow the reaction (runs 1 and 7–10). The reaction is -0.1 order in ligand concentration. The reaction is first order in the Rh concentration up to 1.0 mM (runs 1 and 11–15); however, the reaction rate became constant regardless of the Rh concentration above 1.0 mM (runs 16–18). The isoselectivity and enantioselectivity are constant in runs 1 and 11–15, whereas, at Rh concentrations above 1.0 mM, both the isoselectivity and %ee of isoaldehyde decline. Thus, at higher Rh concentrations, another, possibly multinuclear,⁶ species may be formed that is less active and less selective. A rhodium carbonyl species, complex **10**, has been observed in the decomposition of rhodium hydride **2** (vide infra). The effect of styrene concentration has also been investigated. The H₂ and CO pressures were kept constant, and the reaction was followed by IR, Figure 4a. A plot of [styrene]^{(1-x)/(1-x)} against time is linear when $x = 0.6$ (Figure 4b). The selectivity is not affected by the initial styrene concentration; thus, under otherwise the same conditions as run 1, an isoselectivity of 91.1% and %ee of the isoaldehyde of 94.1 and 94.9%, respectively, were observed when the reaction was started with either 0.10 or 0.010 M of styrene. The fact that the selectivities are independent of the initial styrene concentration suggests that the active species is the same regardless of the styrene concentration. In other words, during the hydroformylation reaction, the active species are not affected by the styrene consumption, as long as the Rh concentration is kept below 1.0 mM. Summarizing all the kinetic data, the hydroformylation rate with **2b** at 60 °C can be described by $r_{obs} = k_{obs}[\text{Rh}]^{1.0}[\text{styrene}]^{0.6}[\text{1b}]^{-0.1}P_{CO}^{-0.9}$, where k_{obs} is a constant, in good agreement with the equation proposed by van Leeuwen, rate = $A[\text{Rh}][\text{alkene}]/\{B[\text{CO}] + C[\text{alkene}] + [\text{ligand}]\}$.⁸ This equation is appropriate for a reaction in which the overall rate is determined by the alkene coordination/hydride migration step. Thus, in the Wilkinson's dissociative mechanism described in Scheme 2, the reaction rate is mostly controlled by (1) the equilibrium between the resting state **2** and its decarbonylated counterpart **3** and (2) the styrene coordination/hydride migration steps, i.e., **3** to **4** or **5**.

Activation Energy for the Hydroformylation. As mentioned above, a consideration of the various order of the reaction allows us to ascribe the rate-determining step to the equilibrium between **2** and **3** and bimolecular reaction of **3** with styrene. The temperature dependency of r_{obs} was measured for catalysts **2a** and **2b**, and the results are summarized in Table 4. If the temperature dependency of H₂ and CO solubilities in benzene and the temperature dependency of the equilibrium between **2** and **3** are neglected, the apparent activation energy E_a from **3** to **4** or to **5** can be estimated from the Arrhenius plot shown in Figure 5 and is found to be 20.0 kcal/mol for the reaction using **2b** and 18.5 kcal/mol for **2a**. These values are comparable to those previously reported for hydroformylation with other

Table 2. Effect of H₂/CO Total Pressure on Preparation of 2b, Styrene Introduction, and Hydroformylation^a

run	H ₂ /CO (1:1) total pressure (atm)			selectivities	
	preparation of 2b	addition of styrene	hydroformylation	isoselectivity % ^b	%ee of iso
1 ^c			20	93.5	94.9
2 ^d			20	93.3	95.3
3	20	1	20	92.6	95.3
4	20	20	20	92.2	95.5
5	70	1	20	91.5	82.5
6 ^e	70	1	20	91.5	94.8
7	70	20	20	93.0	95.6
8	70	70	70	93.3	95.0
9	70	1	70	93.7	95.3

^a [Rh(acac)(CO)₂] = 1.0 mM, [**1b**] = 4.0 mM, [styrene]₀ = 0.010 M, 60 °C in 10 mL of benzene. The reaction was carried out either with a mixture of Rh(acac)(CO)₂ and **1b** (runs 1 and 2) or with **2b** preformed prior to the introduction of styrene (runs 3–9). For the preparation of **2b**, a mixture of Rh(acac)(CO)₂ and **1b** was treated with H₂/CO under a total pressure of 20 or 70 atm for 2 h at 40 °C unless otherwise stated. ^b Determined by GC, not by ¹H NMR. ^c Styrene was added to a Rh(acac)(**1b**) solution under argon. ^d Styrene was added to a Rh(acac)(**1b**) solution under air. ^e Preparation of **2b** for 0.5 h instead of 2 h.

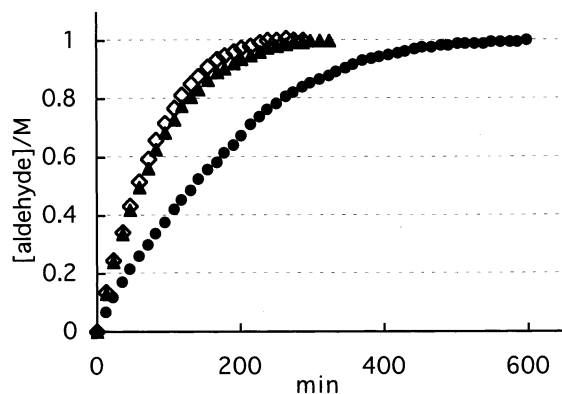


Figure 3. Increase of aldehyde concentration in the asymmetric hydroformylation with **2a–c**: ● **2a**, ◇ **2b**, ▲ **2c**. Conditions: [**2**] = 1.0 mM, free **1** = 3.0 mM, [styrene]₀ = 1.0 M, P_{H_2-0} (the initial H₂ pressure) = P_{CO-0} (the initial CO pressure) = 10 atm, 60 °C, benzene solution (total 20 mL). Aldehyde production rates $r_{obs} = 6.3 \times 10^{-5} \text{ M}\cdot\text{s}^{-1}$ (**2a**), $14.9 \times 10^{-5} \text{ M}\cdot\text{s}^{-1}$ (**2b**), and $14.7 \times 10^{-5} \text{ M}\cdot\text{s}^{-1}$ (**2c**) were calculated in the region of conversion 0–40%.

Table 3. Effect of H₂ and CO Pressures and Rhodium and Ligand 1b Concentrations on the Reaction Rate^a

run	P_{H_2-0}/P_{CO-0} (atm)	[Rh] ₀ (mM)	[1b] ₀ (mM)	isoselect. (%)	%ee of iso-	$r_{obs} \times 10^5$ (M/s)
1	10/10	1.0	4.0	89.2	94.8	14.9
2	80/10	1.0	4.0	89.1	94.5	15.3
3	10/15	1.0	4.0	91.4	95.1	6.98
4	10/20	1.0	4.0	91.4	94.7	5.39
5	10/40	1.0	4.0	92.0	95.5	3.29
6	10/80	1.0	4.0	91.8	95.5	1.60
7	10/10	1.0	6.0	90.2	95.2	13.8
8	10/10	1.0	8.0	90.3	95.1	12.9
9	10/10	1.0	12.0	89.9	94.8	12.7
10	10/10	1.0	16.0	90.3	94.8	12.3
11	10/10	0.10	0.40	90.2	93.4	1.26
12	10/10	0.25	1.00	90.9	95.1	2.81
13	10/10	0.38	1.50	91.6	95.3	5.42
14	10/10	0.50	2.0	90.5	95.2	9.79
15	10/10	0.75	3.0	89.8	94.7	15.2
16	10/10	1.5	6.0	87.4	93.4	15.4
17	10/10	2.0	8.0	85.0	92.3	15.9
18	10/10	4.0	16.0	77.9	87.8	13.4

^a Conditions: [styrene]₀ = 1.0 M, 60 °C, benzene solution (total 20 mL). A reaction rate was measured in conversion 0–40%.

systems, which are in the range 13–22 kcal/mol for either rate-determining hydrogenolysis or alkene coordination/hydride migration.^{12,19–21}

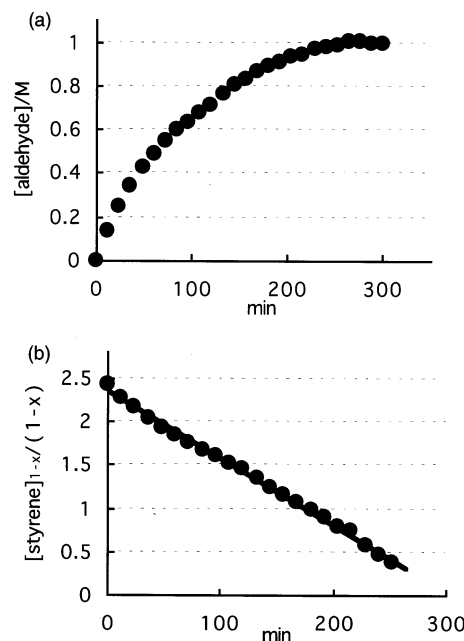


Figure 4. (a) Effect of styrene concentration. Conditions: [**2b**] = 1.0 mM, free **1b** = 3.0 mM, [styrene]₀ = 1.0 M, $P_{H_2} = P_{CO} = 10$ atm (constant), 60 °C, benzene solution (total 20 mL). For the product, isoselectivity was 91.6% with 94.9% ee. (b) Integration of the equation “ $-d[\text{styrene}]/dt = k[\text{styrene}]^{1-x}$ ” provides us with the equation “ $[\text{styrene}]^{1-x}/(1-x) = -kt + A$ (A : a constant) ($x \neq 1$)”. Shown here is a linear plot of $[\text{styrene}]^{1-x}/(1-x)$ vs time when $x = 0.6$. Thus, the reaction is regarded as 0.6th order to styrene concentration.

Observation of the Rhodium Carbonyl Species

10. When a concentrated solution of the rhodium hydride **2b** was treated with a high CO pressure in the absence of styrene, the IR absorption characteristic of a Rh–H disappeared. Thus, **2b** was prepared by treatment of Rh(acac)(CO)₂/**1b** (1:2, [Rh] = 50.0 mM in benzene) with H₂/CO (10 atm/10 atm) at 40 °C for 4.6 h. The pressure was then released to 1 atm, and H₂

(18) Below a CO pressure of 0.5 atm, %ee decreased in our previous study.¹⁶

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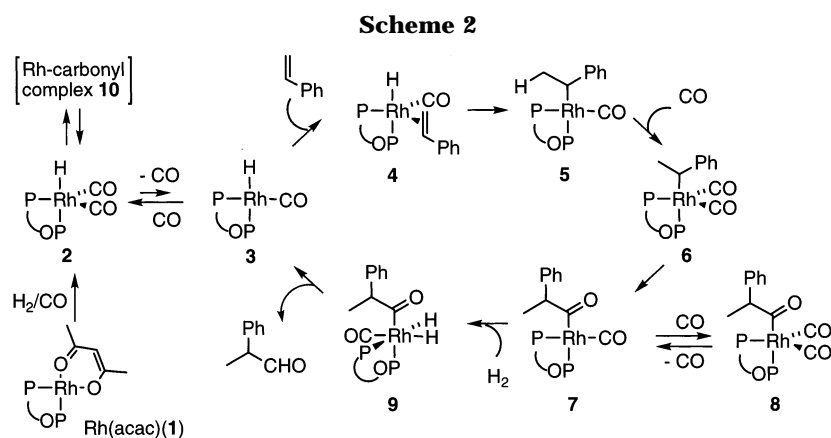
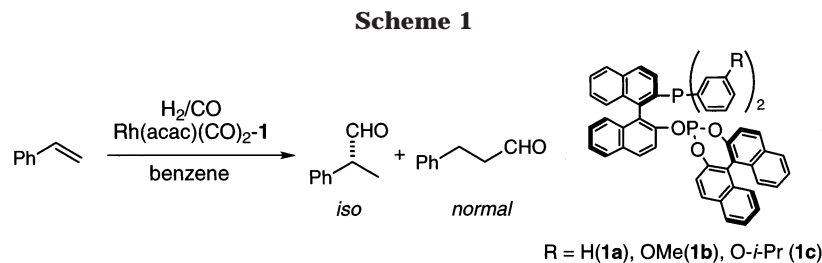


Table 4. Reaction Rate Constant r_{obs} of the Asymmetric Hydroformylation of Styrene under Various Temperatures^a

catalyst	temp (°C)	isoselect. (%)	%ee of iso	$r_{\text{obs}} \times 10^5$ (M/s) ^a
2a	20	91.1	94.6	0.149
	30	89.8	94.9	0.413
	45	88.4	93.7	2.00
	60	87.2	92.5	6.29
2b	20	95.8	97.5	0.254
	30	94.3	96.8	0.675
	45	93.2	95.7	3.64
	60	89.3	95.2	14.9

^a Conditions: [styrene]₀ = 1.0 M, [**2b**] = 1.0 mM, [free **1b**] = 3.0 mM, $P_{\text{H}_2} = P_{\text{CO}} = 10$ atm (constant), benzene solution (total 20 mL). A reaction rate was measured in conversion 0–40%.

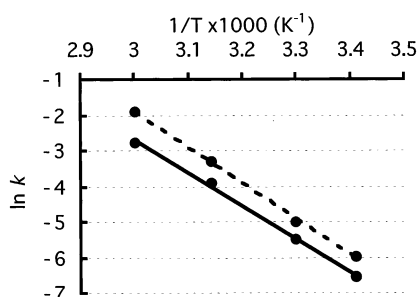


Figure 5. Arrhenius plot for the reactions with (---) **2a** and (—) **2b**. When the equation $\ln k = (-E_a/R)(1/T) + \ln A$ (A : frequency factor, E_a : activation energy, $R = 1.987$ cal/mol·K) is applied, with **2a**: $\ln k = -9.32(1/T) + 25.3$, $E_a = 18.5$ kcal/mol; and with **2b**: $\ln k = -10.0(1/T) + 28.2$, $E_a = 20.0$ kcal/mol.

introduced to a pressure of 10 atm. To this, CO was added stepwise. The IR spectrum was recorded at CO partial pressures of 5, 10, 20, and 35 atm, Figure 6. The peak at 2043 cm^{-1} (Rh–H) decreased with increasing P_{CO} , while the peaks at 1968 (Rh–CO) and 2013 (Rh–CO) cm^{-1} increased. The absorptions changed immediately after each pressure change. Although a

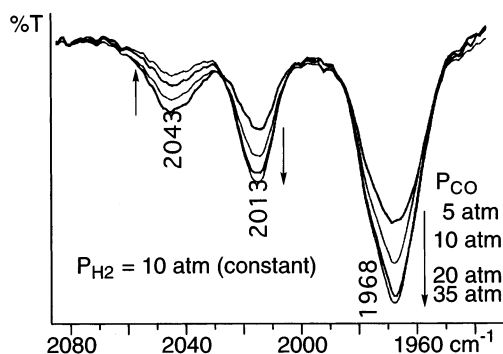


Figure 6. Formation of rhodium carbonyl **10b** from **2b**. To a benzene solution of **2b** (**2b**) = 50.0 mM, [free **1b**] = 50.0 mM) first H_2 was introduced to its partial pressure of 10 atm, and to this, CO was added stepwise. The IR absorption was recorded at the CO partial pressures of 5, 10, 20, and 35 atm. The peaks at 1968 and 2013 cm^{-1} increased, while that at 2043 cm^{-1} decreased.

carbonyl-bridged Rh dimer is a possible candidate for this new species, the low signal/noise ratio did not allow us to characterize any peaks below 1800 cm^{-1} , i.e., in the bridging carbonyl region.^{22,23} We therefore ascribe the species to the rhodium carbonyl complex **10b** of unknown structure. The conversion of **2b** to **10b** was reversible. When a solution of **2b** prepared as above under $P_{\text{H}_2} = P_{\text{CO}} = 10$ atm was further pressurized with H_2 to $P_{\text{H}_2} = 80$ atm and $P_{\text{CO}} = 10$ atm, a slight increase in the Rh–H absorption was detected. Thus, solutions of **2b** prepared under 20 atm are likely to contain **10b** to some extent, at least at a Rh concentration of 50 mM. We cannot exclude the possibility that a solution of **2b** might contain some **10b**, even at Rh concentrations below 1.0 mM. However, the fact that the selectivities are independent of [Rh] below 1.0 mM allows us to

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(23) Moasser, B.; Gladfelter, W. L. *Organometallics* **1995**, *14*, 3832.

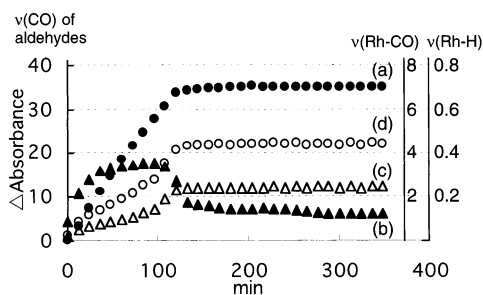


Figure 7. Time dependency of absorbance of (●) aldehydes $\nu(\text{CO})$ 1726 cm^{-1} (plot a), (▲) $\nu(\text{Rh-H})$ at 2044 cm^{-1} (plot b), (△) $\nu(\text{CO})$ at 2013 cm^{-1} (plot c), and (○) $\nu(\text{CO})$ at 1969 cm^{-1} (plot d) for the real time observation of asymmetric hydroformylation of styrene with $\text{Rh}(\text{acac})(\mathbf{1a})$. Conditions: $[\text{Rh}(\text{acac})(\mathbf{1a})] = 34.2\text{ mM}$, $[\text{free } \mathbf{1a}] = 34.2\text{ mM}$, $[\text{styrene}]_0 = 2.74\text{ M}$, $P_{\text{H}_2} = P_{\text{CO}} = 20\text{ atm}$ (constant), in benzene (total 14.6 mL), at $40\text{ }^\circ\text{C}$. For the y axis, the scale on the left side corresponds to aldehyde $\nu(\text{CO})$ and the right side corresponds to either $\nu(\text{Rh-H})$ or $\nu(\text{Rh-CO})$.

estimate that, even if it is present, the contribution of **10b** to the reaction is not significant at Rh concentrations below this level.

Real Time Observation of Styrene Hydroformylation. The asymmetric hydroformylation of styrene with $\text{Rh}(\text{acac})(\text{CO})_2\mathbf{1a}$ was followed by HPIR. In the presence of $\text{Rh}(\text{acac})(\text{CO})_2\mathbf{1a}$ (1:2), a benzene solution of styrene was treated with H_2 and CO at $40\text{ }^\circ\text{C}$. The intensities of the absorptions due to aldehydes $\nu(\text{CO})$ at 1726 cm^{-1} , $\nu(\text{Rh-H})$ at 2044 cm^{-1} , $\nu(\text{Rh-CO})$ at 2013 cm^{-1} , and $\nu(\text{Rh-CO})$ at 1969 cm^{-1} are plotted in Figure 7 against reaction time. Because of the limited signal/noise ratio, this experiment was carried out at a high concentration of Rh (34.2 mM) compared to the standard hydroformylation reaction (cf. Table 3, runs 1 and 11–18). The absorption at 2044 cm^{-1} is due to $\nu(\text{Rh-H})$ of **2a**, and those at 2013 and 1969 cm^{-1} are attributable to the sum of **2a** and **10a** (vide supra). Here we remark on the following two features: (1) When the aldehyde production rate is greatest, the concentration of **2a** reaches its highest value. Thus, apparently, the concentration of the hydride complex **2a** reflects the concentration of the active species. (2) When styrene is completely consumed, the absorptions of the hydride complex **2a** become almost invisible and the rhodium carbonyl species **10a** becomes the only detectable Rh complex. The following two explanations are possible: (1) As the olefin concentration decreases, the concentration of coordinatively unsaturated **3a** increases. **3a** might then react with **2a** to give **10a**. (2) Slow spontaneous formation of **10a** occurs. In this a case, **2a** is presumably first formed and then converted to **10a** during the reaction.

As another species to start the hydroformylation, we attempted to prepare the acyl complex **8b**. The infrared absorption of **2b** at 2043 cm^{-1} (Rh-H stretching) disappears immediately when styrene (1.0 M) and CO (10 atm) were added to a solution of rhodium hydride **2b** (40.7 mM) in that absence of H_2 , suggesting the styrene insertion to the Rh-H bond occurred. Three new absorptions appeared at 2016 , 1972 , and 1960 cm^{-1} . Similarly, peaks were observed at 2011 , 1971 , and 1961 cm^{-1} for the analogous reaction with **2a**. We attribute these absorptions to the acyl complexes **8b** and **8a**;

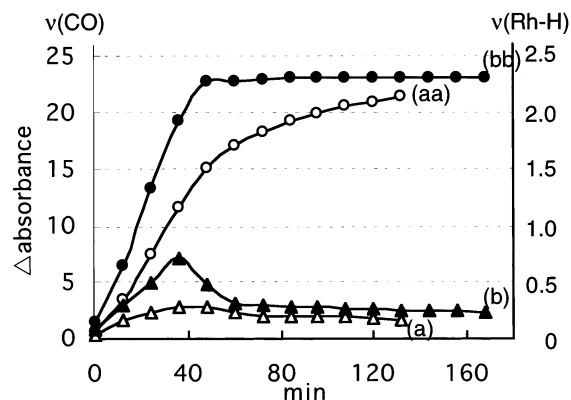


Figure 8. Time dependency of absorbance of aldehydes ($\nu(\text{CO})$: 1726 cm^{-1}) with (○) **2a** (plot aa) and (●) **2b** (plot bb); and absorbance of **2** ($\nu(\text{Rh-H})$) of (▲) **2a** [$\nu(\text{Rh-H})$] at 2046 cm^{-1} , plot a) and (△) **2b** [$\nu(\text{Rh-H})$] at 2044 cm^{-1} , plot b). For the y axis, the scale on the left side corresponds to aldehyde $\nu(\text{CO})$ and the right side corresponds to $\nu(\text{Rh-H})$. Applied conditions are $[\mathbf{8}] = 40.7\text{ mM}$, $[\text{free } \mathbf{1}] = 40.7\text{ mM}$, $[\text{styrene}]_0 = 1.63\text{ M}$, $P_{\text{H}_2} = P_{\text{CO}} = 20\text{ atm}$ (constant), in benzene (total 12.3 mL), at $40\text{ }^\circ\text{C}$.

however, the low signal/noise ratio of the spectra did not allow us to measure the region below 1800 cm^{-1} to confirm the presence of acyl carbonyl absorptions. Although the acyl complex **8b** has not been fully characterized, this mixture was employed as a catalyst precursor and was pressurized with H_2 to initiate the reaction. The production and decay of the resting state **2b** were observed as described above, Figure 8, plot b. A similar behavior is observed for **2a** starting from **8a**, Figure 8, plot a. As a reference, aldehyde formation is also plotted in the same graph, plot aa for the reaction using **8a** and **8b** (bb). It should be noted that the highest concentration of **2b** is 2.5 times greater than that of **2a**, indicating that the concentration of the active species is 2.5 times higher with **1b** than with **1a**. This difference in the position of the equilibrium between **2** and **10** is a possible explanation for the faster reaction with **2b** than with **2a**, even under low Rh-concentration conditions.

Conclusion

Introduction of MeO and *i*-PrO groups into (*R,S*)-BINAPHOS results in the acceleration of the reaction as well as an improvement in the regio- and enantioselectivities. Kinetic studies have clarified the detailed mechanism; in particular, the equilibrium between **2** and **3** and styrene coordination/hydride migration control the reaction rate. The faster reaction using **1b** is attributed to the higher concentration of **3** (reflected by **2**) under the catalytic conditions. The steric repulsion between the MeO group and the carbonyl might be responsible for either the acceleration of CO dissociation from **2** or the deceleration of CO re-coordination to **3**; however, the possibility of an electronic effect cannot be excluded. More importantly, the existence of a rhodium carbonyl species **10** at Rh concentrations above 1.0 mM is associated with a decline in both activity and enantioselectivity, compared with **2**, in the asymmetric hydroformylation of styrene. The concentration of **10** was observed to increase as the olefin is consumed by real-time in situ IR spectroscopy, especially when high concentrations of rhodium are used.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive compounds were carried out using standard Schlenk techniques under argon purified by passing through a hot column packed with BASF-Catalyst R3-11. The in situ infrared spectra were recorded on an ASI, REACT IR 1000 equipped with a silicon probe. All NMR spectra were measured using a Varian Mercury 200 (^1H 200 MHz; ^{31}P 81 MHz) spectrometer. Tetramethylsilane (^1H) and H_3PO_4 (^{31}P) were employed as internal and external standards, respectively. Gas chromatographic (GLC) analyses were conducted on a Shimadzu GC-2010 equipped with a flame ionization detector. Optical rotation was measured on a JASCO DIP-360. Melting points were measured on a Yanagimoto-Seisakusho micro melting point apparatus, MD-500D. Elemental analyses were performed at the Microanalytical Center, Kyoto University. Most reagents were purchased from Wako Pure Chemical Industries Ltd., or Aldrich Chemical Co., Inc., and benzene was purified by distillation over sodium benzophenone ketyl under argon. Styrene, vinyl acetate, 1-hexene, and indene were purified by distillation in vacuo. Carbon monoxide, hydrogen, and carbon monoxide/hydrogen gas mixture (50.1%/49.9%) were obtained from Teisan CO.

General Procedure for the Asymmetric Hydroformylation of Olefins Catalyzed by Rhodium(I) Complexes of BINAPHOS Derivatives. A procedure similar to our previous report was employed.² A solution of styrene (1.04 g, 10.0 mmol), $\text{Rh}(\text{acac})(\text{CO})_2$ (1.3 mg, 5.0 μmol), and **1a** (15.4 mg, 0.020 mmol) in benzene (0.5 mL) was treated with carbon monoxide (10 atm) and hydrogen (10 atm) at 60 °C for 20 h. Conversion to aldehydes (>99%) and the regioselectivity of the reaction (2-phenylpropanal/3-phenylpropanal, 88.0:12.0) were determined by ^1H NMR spectroscopy of the crude reaction mixture without evaporation of the solvent. The enantiomeric excess of the 2-phenylpropanal was determined to be 93.2% by oxidation of 2-phenylpropanal to the corresponding carboxylic acid. An aliquot of the aldehydes mixture was dissolved in acetone, and to this, Jones reagent ($\text{CrO}_3/\text{H}_2\text{SO}_4$, $[\text{Cr}] = 2.67 \text{ M}$) was added until the color does not change from orange to green. After extraction, the ee of carboxylic acid was determined by GLC analysis using a chiral capillary column (Chirasil-DEX CB, 0.25 mm \times 25 m, 150 °C, He 1.4 kg $\cdot\text{cm}^{-2}$). Other olefins were subjected to hydroformylation by the same procedure. The ee's of 2-methylheptanal, 2,3-dihydro-1*H*-indene-1-carboxaldehyde, and 2-methylbutyraldehyde were determined by Jones oxidation followed by GLC analysis using the same capillary column (110, 150, and 90 °C, respectively). The ee of 3-acetoxy-2-methylpropanal was determined by GLC analysis using the same capillary column without oxidation (50 °C). The ee of α -methyl-2-naphthaleneacetaldehyde and *N*-acetyl-2-methyl-3-oxo-D-alanine methyl ester was determined by ^1H NMR using $\text{Eu}(\text{hfc})_3$. As a reference, blank experiments were performed as follows. When a solution of styrene (6 mmol) and $\text{Rh}(\text{acac})(\text{CO})_2$ (0.8 mg, 3 μmol) in

benzene (0.3 mL) was treated with carbon monoxide (10 atm) and hydrogen (10 atm) at 60 °C for 20 h, conversion of styrene was 33%, suggesting the slower reaction in the absence of **1a**. The regioselectivity was 2-phenylpropanal/3-phenylpropanal = 68.6:31.4. At 25 °C for 22 h in the absence of **1a**, the conversion of styrene was 0.3%.

General Procedure for Kinetics Studies. A solution of $\text{Rh}(\text{acac})(\text{CO})_2$ (5.4 mg, 0.020 mmol) and **1b** (66.3 mg, 0.080 mmol) in benzene (10 mL) was degassed by freeze-pump-thaw cycles and transferred into a 100 mL stainless steel autoclave equipped with a silicon IR probe and a magnetic stirrer. Carbon monoxide (35 atm) and hydrogen (35 atm) were charged, and the solution was stirred at 60 °C for 30 min with an agitation speed of 800 rpm. After depressurization, a degassed mixture of styrene (2.08 g, 20 mmol) and benzene (total 10 mL) was added. The autoclave was put under a pressure of carbon monoxide (10 atm) and hydrogen (10 atm) at 40 °C stirring with 800 rpm, and IR spectra were recorded. Recording was started 30 s after the gas was added. To calculate the reaction rate, the intensity of the absorption peak at 1726 cm^{-1} was converted to the aldehyde concentration on the basis that the saturated absorption corresponds to 1.0 M (100% conversion to aldehyde).

General Procedure for the Observation of Rh Complexes. In a 100 mL stainless steel autoclave equipped with a silicon probe and a magnetic stirrer, a solution of $\text{Rh}(\text{acac})(\text{CO})_2$ (129 mg, 0.50 mmol) and **1b** (829 mg, 1.0 mmol) in benzene (10 mL) was pressurized with carbon monoxide (20 atm) and hydrogen (20 atm), and the solution was stirred with an agitation speed of 800 rpm at 40 °C. Recording of IR spectra was started when gases were added.

Preparation of Phosphine-Phosphite Ligands 1b and 1c. Ligands are readily accessible from commercially available aryl bromides, 3-methoxybromobenzene, and 3-(2-propoxy)-bromobenzene for **1b** and **1c**, respectively, according to the reported procedures.² **1b**: white solid, mp 165.1–166.4 °C (benzene). ^{31}P NMR (CDCl_3): δ -11.8 (phosphine, $J_{\text{P-P}} = 38.1 \text{ Hz}$), 145.0 (phosphite); $[\alpha]_{\text{D}}^{25}$ 163 (*c* 0.48, CH_2Cl_2). Anal. Calcd for $\text{C}_{54}\text{H}_{38}\text{O}_5\text{P}_2$: C, 78.25; H, 4.62. Found: C, 77.95; H, 4.73. **1c**: white solid, mp 174.5–176.0 °C (benzene). ^{31}P NMR (CDCl_3) δ -12.0 (phosphine, $J_{\text{P-P}} = 45.8 \text{ Hz}$), 145.2 (phosphite); $[\alpha]_{\text{D}}^{25}$ 133 (*c* 0.52, CH_2Cl_2). Anal. Calcd for $\text{C}_{58}\text{H}_{46}\text{O}_5\text{P}_2$: C, 78.72; H, 5.24. Found: C, 78.47; H, 5.42.

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Supporting Information Available: Original plots of reaction rate varying H_2 and CO pressures, Rh and ligand concentrations, and temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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