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Asymmetric Ligand-Exchange Reaction of Biphenol Derivatives and Chiral Bis(oxazolinyl)phenyl–Rhodium Complex

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: Chiral bis(oxazolinyl)phenyl–rhodium acetate complex can enantioselectively capture 1,1′-binaphthol derivatives by ligand-exchange reaction. The structure of the bis(oxazolinyl)phenyl–rhodium biphenol and binaphthol complexes were confirmed by X-ray analysis.

Keywords: binaphthols · enantioselectivity · ligand exchange · oxazolines · rhodium

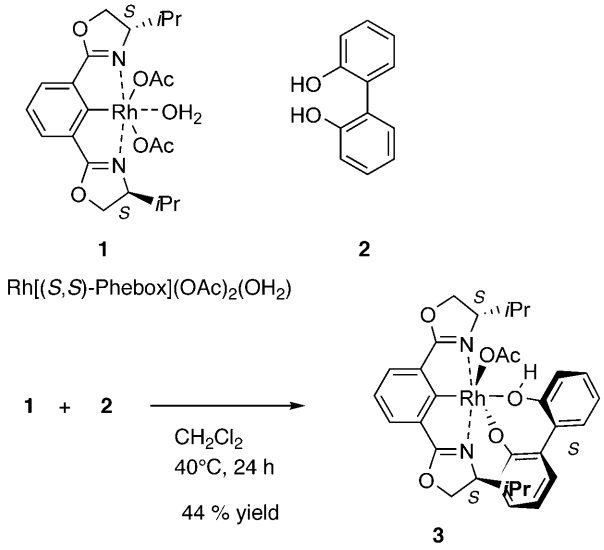
Introduction

We previously demonstrated that chiral bis(oxazolinyl)phenyl (Phebox) ligands are potent terdentate NCN ligands that provide a chiral meridional coordination site and a C_2-symmetric environment, the transition-metal complexes of which have been applied to asymmetric catalysis.[1] Recently, we found that the acetate group on the Rh complexes play a key role as a basic site for cleavage of the C–H bond of aromatic compounds, acetylenes, and ketones.[2] On the basis of these observations, we envisioned the possibility of a ligand-exchange reaction between the acetate ligand and certain phenols in terms of molecular recognition of chiral molecules around the transition-metal coordination sites. After screening some phenol compounds, we found that 2,2′-biphenol and 1,1′-bi(2-naphthol) derivatives can exchange to form biphenolate or binaphtholate derivatives. Herein, we reveal some ligand-exchange reactions, including enantioselective reactions and kinetic resolution of binaphthol derivatives, which are important chiral reagents for asymmetric synthesis and molecular recognition.[3,4]

Results and Discussion

Reaction of Rh[(*S*,*S*)-Phebox] Acetate 1 and 2,2′-Biphenol (2)

First, we attempted a ligand-exchange reaction with 2,2′-biphenol (**2**). A solution of rhodium complex **1** and **2** (1.5 equiv) in CH_2Cl_2 was stirred for 24 h at 40 °C. The mixture was purified by silica-gel column chromatography with hexane/ethyl acetate to give Rh[(*S*,*S*)-Phebox](biphenolate)(OAc) **3** in 44 % yield (Scheme 1).[5] In toluene, complex **3** was isolated in 47 % yield at 40 °C and in 55 % yield at



Scheme 1. Ligand-exchange reaction of Rh[(*S*,*S*)-Phebox] acetate **1** and 2,2′-bi(2-phenol) (**2**).

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70 °C. Interestingly, X-ray analysis of **3** shows that the biphenol moiety is fixed in the axially chiral form with the absolute configuration of *S* on the rhodium complex, although biphenol **2** is an achiral molecule (Figure 1). The corresponding rhodium complex bearing the *R* biphenol could not be detected under the above conditions. It is thought that the complex with the *R* biphenol may be too unstable to isolate by silica-gel chromatography or TLC monitoring at ambient temperature.

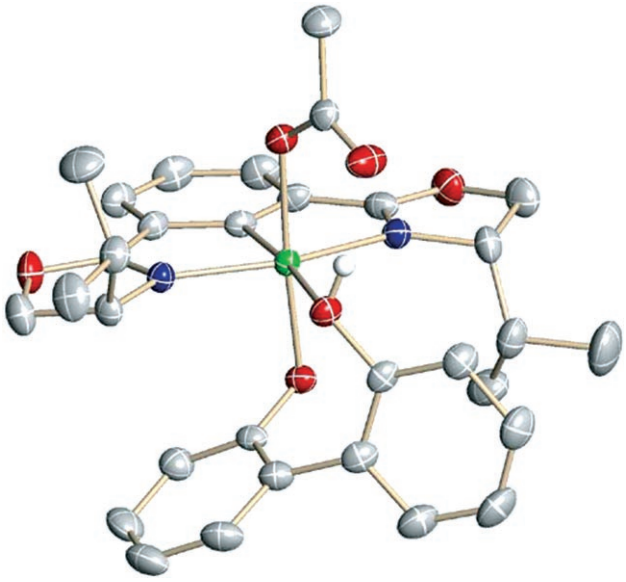


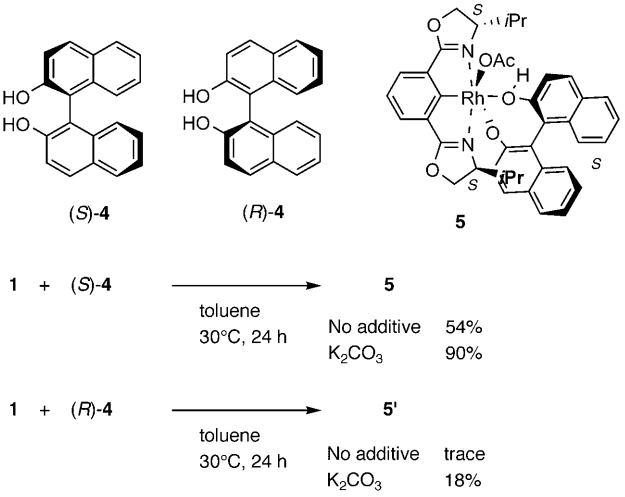
Figure 1. Molecular structure of Rh[(*S*,*S*)-Phebox](biphenolate)(OAc) **3**.

Reaction of Rh[(*S*,*S*)-Phebox] Acetate 1 and 1,1′-Bi(2-naphthol) (4)

On the basis of the above finding that the Rh[(*S*,*S*)-Phebox] fragment captures favorably the *S* form of the biphenol skeleton, we envisioned that *S* binaphthol (*S*)-**4** rather than (*R*)-**4** would bind strongly to Rh[(*S*,*S*)-Phebox]. A solution of rhodium complex **1** and (*S*)-**4** (1.5 equiv) in toluene was stirred for 24 h at 30 °C. The mixture was purified by silica-gel column chromatography with hexane/ethyl acetate to give Rh[(*S*,*S*)-Phebox](*S* binaphtholate)(OAc) **5** in 54% yield (Scheme 2). The yield increased to 90% by addition of K_2CO_3 (3 equiv), which accelerated the ligand-exchange reaction. On the other hand, the reaction of **1** with (*R*)-**4** gave no stable complex. Use of K_2CO_3 with (*R*)-**4** gave the labile complex **5′** in 18% yield as the desired complex, but its structure could not be determined.

Abstract in Japanese:

キラル（ビスオキサゾリニル）フェニルロジウムアセテート錯体が、配位子交換反応によってエナンチオ選択的にビナフトール類を捕捉することを見いだし、錯体の構造解析に成功した。



Scheme 2. Ligand-exchange reactions of Rh[(*S*,*S*)-Phebox] acetate **1** and 1,1′-bi(2-naphthol) (**4**).

Thus, we found that the chiral Rh[(*S*,*S*)-Phebox] moiety captures (*S*)-1,1′-bi(2-naphthol) selectively to make a relatively stable complex by a ligand-exchange reaction. The structure of **5** was confirmed by X-ray analysis (Figure 2). One of the naphthalene groups is parallel to the oxazoline plane, whereas the other is stacked on the isopropyl group.

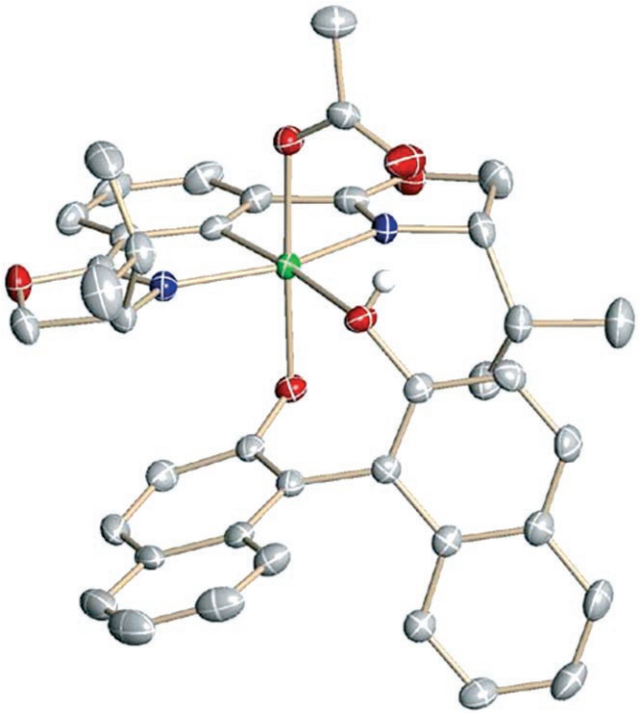
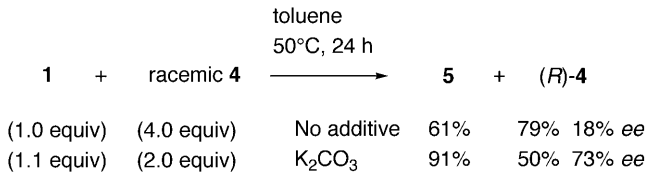


Figure 2. Molecular structure of Rh[(*S*,*S*)-Phebox](*S* binaphtholate)-(OAc) **5**.

Enantiodiscrimination of 1,1′-Bi(2-naphthol)

By using an excess of racemic 1,1′-bi(2-naphthol) (**4**; 4.0 equiv with respect to **1**), the ligand-exchange reaction

with **1** was performed in toluene at 50 °C for 24 h because of the slow exchange rate (Scheme 3). After chromatographic separation with silica gel, complex **5** was obtained in 61 % yield based on **1**. Binaphthol **4** was recovered in 79 % yield based on **4**, with 18 % *ee* (*R*). Treatment of the isolated complex **5** in methanol and hydrochloric acid at room temperature for 10 min gave the optically pure *S* binaphthol and Rh-[(*S*,*S*)-Phebox]$Cl_2(H_2O)$, respectively, in quantitative yields. At reaction temperatures of 60 and 70 °C, the yield of **5** increased to 75 and 85 % based on **1**, respectively.



Scheme 3. Ligand-exchange reactions and kinetic resolution.

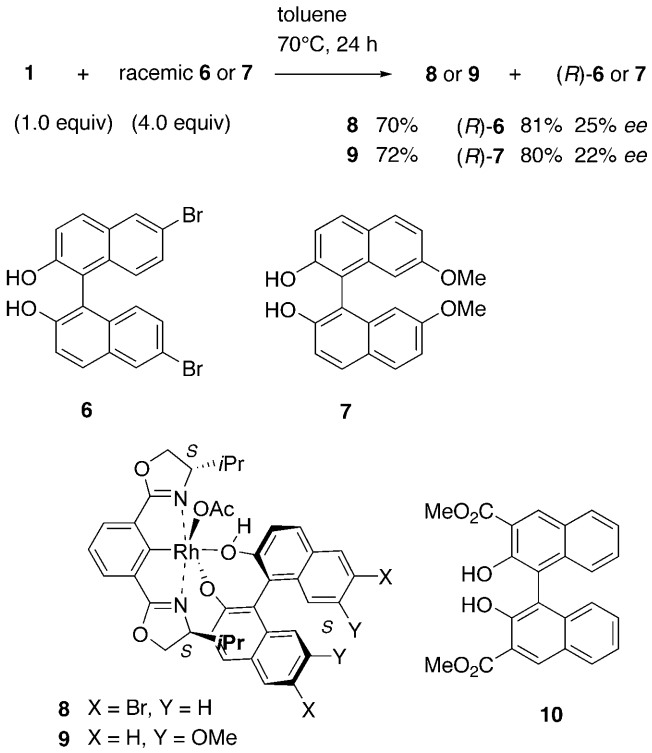
In the presence of K_2CO_3 (0.050 mmol), the ligand-exchange reaction with **1** (0.055 mmol) and racemic **4** (0.10 mmol) proceeded to give complex **5** in around 91 % yield, which was contaminated with a small amount of free binaphthol or the isomeric complex **5′**, and the *R* binaphthol was recovered in 50 % yield with 73 % *ee*. The *S* binaphthol obtained from the mixture of the complexes showed 93 % *ee*. Thus, the addition of K_2CO_3 accelerated the exchange reaction, but it resulted in the formation of an undesirable complex.

Reaction of Rh[(*S*,*S*)-Phebox] Acetate 1 and Substituted 1,1′-Bi(2-naphthol)

Other racemic substituted binaphthols **6** and **7** were examined to produce the corresponding complexes **8** and **9** with *S* binaphthols as ligands in 70 and 72 % yield, respectively (Scheme 4). Optically pure *S* binaphthols were recovered from **8** and **9**. The molecular structure of **8** was also confirmed by X-ray analysis. On the other hand, 3,3′-methoxycarbonyl derivative **10** did not react with **1** because of the sterically hindered binding sites.

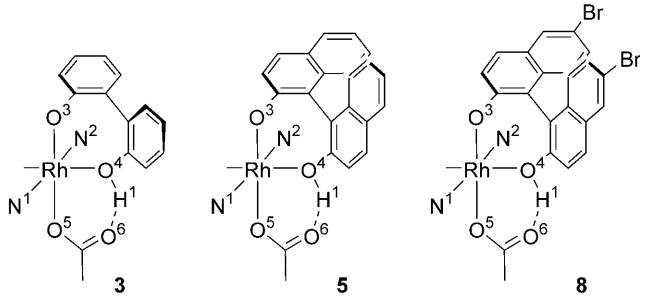
Stabilization of the Complexes by Hydrogen Bonding

We thought that the matched pair of the (*S*,*S*)-Phebox substructure on the rhodium atom and the *S*-binaphthol skeletons could be stabilized mainly by a preferable steric convex–concave stacking relation. Furthermore, it is also interesting that hydrogen bonding between an O atom of the acetate and the H atom of the equatorial OH group of binaphthol was found; this hydrogen bonding may stabilize the complexes. The hydrogen-bond distances $O_{Ac}\cdots H_{OH}$ derived from X-ray analysis are 1.69–1.86 Å for **3**, **5**, and **8** (Table 1).



Scheme 4. Ligand-exchange reactions with other substituted binaphthols.

Table 1. Selected bond lengths and distances (Å) of **3**, **5**, and **8**.



Bond	3	5	8
Rh–O3	1.9977(18)	2.0177(17)	2.0044(18)
Rh–O4	2.2480(17)	2.2683(18)	2.293(2)
Rh–O5	2.0706(19)	2.0646(18)	2.0579(19)
Rh–N1	2.066(2)	2.079(2)	2.073(2)
Rh–N2	2.046(2)	2.062(2)	2.057(2)
O4–H1	0.82(4)	0.69(4)	0.71(3)
H1···O6	**1.69**	**1.85**	**1.86**
O4···O6	2.50	2.50	2.54

Conclusions

We have demonstrated enantioselective ligand-exchange reactions with a chiral (bisoxazolinyl)–rhodium fragment to show the selective capturing of *S*-binaphthol compounds and to clarify the molecular structures of the resulting complexes.

Experimental Section

General

Complex **1** was prepared by our previously reported method.[5] Biphenol **2** and binaphthol derivatives **4** and **6** are commercially available. Binaphthols **7** and **10** were synthesized by coupling with CuCl(OH)·TMEDA (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[6] ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on Varian 300 and 500 spectrometers. Infrared spectra were recorded on a JASCO FR/IR-230 spectrometer. High-resolution mass spectrometry was performed on a JOEL JMS-700 spectrometer.

Syntheses

3: Compounds **1** (26.9 mg, 0.050 mmol) and **2** (14.0 mg, 0.075 mmol) were placed in a flask. Under argon atmosphere, dichloromethane (2 mL) was added, and the mixture was stirred at 40 °C for 24 h. The reaction was monitored by TLC; product R_f = 0.4 (hexane/ethyl acetate = 1:1). The mixture was purified by column chromatography (silica gel, hexane/ethyl acetate = 5:1) to give **3** in 44 % yield (14.2 mg, 0.022 mmol). At 40 °C, a solution of **1** (21.5 mg, 0.040 mmol) and **2** (11.2 mg, 0.060 mmol) in toluene (2.0 mL) gave **3** in 47 % yield (12.2 mg, 0.019 mmol). At 70 °C, a solution of **1** (26.9 mg, 0.050 mmol) and **2** (18.6 mg, 0.10 mmol) in toluene (2.0 mL) gave **3** in 55 % yield (17.8 mg, 0.027 mmol). **3**: Yellowish-orange solid; m.p.: 191 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.56 (d, J = 6.9 Hz, 3H), 0.61 (d, J = 6.6 Hz, 3H), 0.68 (d, J = 6.9 Hz, 3H), 0.81 (d, J = 7.2 Hz, 3H), 1.79 (s, 3H), 1.80–1.94 (m, 1H), 2.06–2.17 (m, 1H), 2.58 (ddd, J = 10.1, 6.9, 3.2 Hz, 1H), 4.18 (ddd, J = 9.9, 6.9, 3.6 Hz, 1H), 4.33–4.47 (m, 2H), 4.61–4.74 (m, 2H), 6.63 (d, J = 8.4 Hz, 1H), 6.86–7.23 (m, 8H), 7.42 (d, J = 7.5 Hz, 1H), 7.67 ppm (dd, J = 7.8, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 14.2, 14.5, 19.3, 19.4, 23.6, 29.1, 29.3, 65.9, 68.4, 71.7, 116.1, 119.1, 120.8, 123.2, 125.2, 127.4, 127.5, 128.1, 131.3, 131.5, 131.8, 131.9, 132.1, 134.9, 155.0, 167.1, 170.6 (d, $J_{Rh,C}$ = 4.6 Hz), 171.9 (d, $J_{Rh,C}$ = 4.2 Hz), 185.1, 188.2 ppm (d, $J_{Rh,C}$ = 26.5 Hz); HRMS (FAB): m/z calcd for $C_{32}H_{35}N_2O_6Rh$: 646.1550; found: 646.1559.

5: Compounds **1** (26.9 mg, 0.050 mmol) and (*S*)-**4** (21.5 mg, 0.075 mmol) were placed in a flask. Under argon atmosphere, toluene (2 mL) was added, and the mixture was stirred at 30 °C for 24 h. The reaction was monitored by TLC; product R_f = 0.6 (hexane/ethyl acetate = 1:1). The mixture was purified by column chromatography (silica gel, hexane/ethyl acetate = 4:1) to give **5** in 54 % yield (20.0 mg, 0.027 mmol). With K_2CO_3 (20.7 mg, 0.15 mmol), **5** was obtained in 90 % yield (33.7 mg, 0.045 mmol). **5**: Yellowish-orange solid; m.p.: 226 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.01 (d, J = 6.6 Hz, 3H), 0.33 (d, J = 7.2 Hz, 3H), 0.40 (d, J = 6.9 Hz, 3H), 0.48 (d, J = 6.6 Hz, 3H), 0.70–0.82 (m, 1H), 1.75 (s, 3H), 1.96–2.06 (m, 1H), 2.13–2.19 (m, 1H), 4.05 (ddd, J = 9.9, 6.3, 3.0 Hz, 1H), 4.40–4.61 (m, 4H), 6.60 (d, J = 9.0 Hz, 1H), 6.91 (dd, J = 13.5, 8.4 Hz, 1H), 7.01–7.08 (m, 2H), 7.16–7.25 (m, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.59 (dd, J = 7.5, 1.1 Hz, 1H), 7.67 (dd, J = 7.5, 1.1 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.7 Hz, 1H), 7.92 ppm (d, J = 8.7 Hz, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 13.4, 13.8, 18.9, 19.0, 23.7 (d, $J_{Rh,C}$ = 3.0 Hz), 28.0, 28.9, 66.1 (d, $J_{Rh,C}$ = 3.0 Hz), 68.6, 71.3, 71.8, 118.0, 121.4, 122.2, 123.3, 123.5, 124.9, 125.1, 125.6, 126.0, 127.8, 127.9, 127.9, 128.0, 128.2, 128.4, 128.6, 129.3, 129.9, 130.9, 132.3, 132.6, 135.3, 135.8, 153.4, 167.7, 171.0, 172.0, 185.1, 189.2 ppm (d, $J_{Rh,C}$ = 25.8 Hz); HRMS (FAB): m/z calcd for $C_{40}H_{39}N_2O_6Rh$: 746.1863; found: 746.1876. When (*R*)-**4** was used with K_2CO_3 under the same conditions described above, **5′** was obtained in 18 % yield (6.8 mg, 0.009 mmol).

Enantiodiscrimination: Compound **1** (26.9 mg, 0.050 mmol) and racemic **4** (57.3 mg, 0.20 mmol) were placed in a flask. Under argon atmosphere, toluene (2 mL) was added, and the mixture was stirred at 50 °C for 24 h. The mixture was purified by column chromatography (silica gel, hexane/ethyl acetate = 5:1) to give **5** in 61 % yield (22.7 mg, 0.0304 mmol) and **4** in 79 % yield (45.0 mg, 0.157 mmol; 18 % *ee* (*R*), DAICEL CHIRALPAK AD-H, hexane/*i*PrOH = 90:10, 1.0 mL min^{-1}, t_R = 31.6 (*R*), 36.8 min (*S*)). Next, hydrochloric acid (1 N, 0.5 mL) was added to a solution of **5** (22.7 mg) in methanol (1.5 mL). The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 5:1→0:1) to give (*S*)-**4** in >99 % yield (8.6 mg, 0.030 mmol) and Rh[(*S*,*S*)-Phebox]$Cl_2(H_2O)$ in 96 % yield (14.1 mg, 0.029 mmol). With K_2CO_3 (19.0 mg, 0.14 mmol), a solution of **1** (29.6 mg, 0.055 mmol) and racemic **4** (28.6 mg, 0.10 mmol) in toluene (2 mL) gave **5** in 91 % yield (33.8 mg, 0.0453 mmol; yield based on 0.05 mmol of **4**), and **4** was recovered in 50 % yield (14.4 mg, 0.050 mmol).

8: Compound **1** (26.9 mg, 0.050 mmol) and racemic **6** (88.8 mg, 0.20 mmol) were placed in a flask. Under argon atmosphere, toluene (2 mL) was added, and the mixture was stirred at 70 °C for 24 h. The reaction was monitored by TLC; product R_f = 0.6 (hexane/ethyl acetate = 1:1). The mixture was purified by column chromatography (silica gel, hexane/ethyl acetate = 4:1) to give **8** in 70 % yield (31.7 mg, 0.035 mmol) and recovered **6** in 81 % yield (31.7 mg, 0.035 mmol; 25.3 % *ee* (*R*), DAICEL CHIRALPAK AD-H, hexane/*i*PrOH = 90:10, 1.0 mL min^{-1}, t_R = 21.5 (*R*), 50.1 min (*S*)). **8**: Pale-yellow solid; m.p.: 256 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.01 (d, J = 6.3 Hz, 3H), 0.39 (d, J = 7.2 Hz, 3H), 0.42 (d, J = 6.9 Hz, 3H), 0.48 (d, J = 6.9 Hz, 3 Hz), 0.70–0.84 (m, 1H), 1.66 (br s, 1H), 1.75 (s, 3H), 1.90–2.04 (m, 1H), 2.14–2.22 (m, 1H), 3.99–4.07 (m, 1H), 4.35–4.62 (m, 4H), 6.59 (d, J = 8.7 Hz, 1H), 6.72 (dd, J = 13.7, 9.2 Hz, 2H), 7.11 (ddd, J = 9.2, 6.3, 2.2 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.82 (d, J = 2.1 Hz, 1H), 7.85 (dd, J = 17.4, 9.0 Hz, 2H), 7.99 ppm (d, J = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 13.6, 13.9, 19.1, 19.2, 23.8, 28.2, 29.1, 66.1, 68.5, 71.3, 71.7, 115.5, 116.8, 119.1, 120.8, 123.4, 124.3, 126.6, 126.9, 127.6, 127.7, 127.7, 128.3, 128.5, 129.1, 129.2, 129.3, 129.7, 129.9, 130.6, 131.8, 132.2, 133.3, 133.9, 153.7, 167.9, 170.7, 171.7, 185.0, 188.1 ppm (d, $J_{Rh,C}$ = 26.3 Hz); HRMS (FAB): m/z calcd for $C_{40}H_{37}Br_2N_2O_6Rh$: 902.0073; found: 902.0083.

9: Compound **1** (26.9 mg, 0.050 mmol) and racemic **7** (69.3 mg, 0.20 mmol) were placed in a flask. Under argon atmosphere, toluene (2 mL) was added, and the mixture was stirred at 70 °C for 24 h. The reaction was monitored by TLC; product R_f = 0.63 (hexane/ethyl acetate = 1:1). The mixture was purified by column chromatography (silica gel, hexane/ethyl acetate = 4:1) to give **9** in 72 % yield (29.0 mg, 0.036 mmol) and recovered **7** in 80 % yield (55.2 mg, 0.159 mmol; 21.9 % *ee* (*R*), DAICEL CHIRALPAK AD-H, hexane/*i*PrOH = 90:10, 1.0 mL min^{-1}, t_R = 47.0 (*S*), 52.6 min (*R*)). **9**: Pale-yellow solid; m.p.: 157–160 °C; IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.00 (d, J = 6.6 Hz, 3H), 0.39 (d, J = 6.6 Hz, 3H), 0.42 (d, J = 6.6 Hz, 3H), 0.50 (d, J = 6.6 Hz, 3H), 0.72–0.86 (m, 1H), 1.72 (br s, 1H), 1.75 (s, 3H), 1.96–2.08 (m, 1H), 2.25–2.30 (m, 1H), 3.22 (s, 3H), 3.37 (s, 3H), 4.05 (ddd, J = 9.9, 6.2, 3.0 Hz, 1H), 4.39–4.61 (m, 4H), 6.20 (d, J = 2.4 Hz, 1H), 6.26 (d, J = 2.4 Hz, 1H), 6.45 (d, J = 8.7 Hz, 1H), 6.87 (ddd, J = 12.8, 8.8, 2.6 Hz, 2H), 7.34 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 8.7 Hz, 1H), 7.55 (d, J = 9.0 Hz, 1H), 7.58 (dd, J = 7.5, 0.9 Hz, 1H), 7.67 (dd, J = 7.5, 0.9 Hz, 2H), 7.70 (d, J = 9.3 Hz, 1H), 7.72 (d, J = 8.7 Hz, 1H), 7.81 ppm (d, J = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 13.6, 14.0, 19.1, 19.2, 23.8, 28.1, 29.0, 55.0, 55.1, 66.0, 68.5, 71.3, 71.7, 104.5, 105.0, 113.7, 115.2, 115.3, 120.3, 123.2, 123.8, 124.0, 125.1, 125.7, 127.4, 127.4, 127.5, 128.7, 129.1, 129.3, 131.9, 132.2, 135.9, 136.2, 153.5, 157.3, 157.6, 167.5, 170.5 (d, $J_{Rh,C}$ = 4.0 Hz), 171.6 (d, $J_{Rh,C}$ = 4.1 Hz), 184.5 (d, $J_{Rh,C}$ = 1.2 Hz), 188.7 ppm (d, $J_{Rh,C}$ = 26.3 Hz); HRMS (FAB): m/z calcd for $C_{42}H_{43}N_2O_8Rh$: 806.2074; found: 806.2085.

Crystallographic Structural Determination

3, **5**, and **8**: Single crystals suitable for X-ray diffraction were obtained from pentane/ethyl acetate at room temperature. Diffraction data were collected on a Brucker SMART APEX CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). An empirical absorption correction was applied by using SADABS. Structures were solved by direct methods and refined by full-matrix least squares on F^2 with SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located on calculated positions and refined as rigid groups. **3**: $C_{32}H_{35}N_2O_6Rh$, M_r = 646.53, T = 173(2) K, monoclinic, space group $P2_1$, a = 9.9686(11), b = 9.2537(11), c =

15.9256(18) Å, $\beta = 90.916(2)°$, $V = 1468.9(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.462$ Mg m^{-3}, $\mu = 0.628$ mm^{-1}, $F(000) = 668$, crystal size $= 0.40 \times 0.30 \times 0.20$ mm^3, $\theta = 2.04$–$27.51°$, index ranges: $-12 \le h \le 12$, $-12 \le k \le 7$, $-20 \le l \le 20$; reflections collected: 10383; independent reflections: 4869 (R(int) = 0.0274); completeness to $\theta = 27.51°$, 99.6%; max./min. transmission: 1.000000/0.805557; data/restraints/parameters: 4869/1/379; goodness-of-fit on F^2: 1.065; final R indices ($I > 2\sigma(I)$): $R1 = 0.0247$, $wR2 = 0.0600$; R indices (all data): $R1 = 0.0253$, $wR2 = 0.0605$; largest diff. peak/hole: 0.905/−0.288 e Å^{-3}. **5**: $C_{40}H_{39}N_2O_6Rh$, $M_r = 746.64$, $T = 173(2)$ K, orthorhombic, space group $P2_12_12_1$, $a = 12.686(4)$, $b = 15.603(5)$, $c = 16.958(5)$ Å, $V = 3356.7(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.477$ Mg m^{-3}, $\mu = 0.561$ mm^{-1}, $F(000) = 1544$, crystal size $= 0.50 \times 0.20 \times 0.10$ mm^3, $\theta = 1.77$–$28.35°$, index ranges: $-16 \le h \le 16$, $-20 \le k \le 20$, $-25 \le l \le 22$; reflections collected: 25130; independent reflections: 8350 (R(int) = 0.0508); completeness to $\theta = 28.35°$, 99.7%; max./min. transmission: 1.000000/0.692337; data/restraints/parameters: 8350/0/451; goodness-of-fit on F^2: 1.065; final R indices ($I > 2\sigma(I)$): $R1 = 0.0327$, $wR2 = 0.0735$; R indices (all data): $R1 = 0.0354$, $wR2 = 0.0747$; largest diff. peak/hole: 0.815/−0.389 e Å^{-3}. **8**: $C_{40}H_{37}Br_2N_2O_6Rh$, $M_r = 904.45$, $T = 153(2)$ K, orthorhombic, space group $P2_12_12_1$, $a = 10.239(4)$, $b = 18.720(7)$, $c = 19.609(7)$ Å, $V = 3758(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.598$ Mg m^{-3}, $\mu = 2.630$ mm^{-1}, $F(000) = 1816$, crystal size $= 0.60 \times 0.50 \times 0.30$ mm^3, $\theta = 1.50$–$27.57°$, index ranges: $-13 \le h \le 12$, $-22 \le k \le 24$, $-25 \le l \le 21$; reflections collected: 26413; independent reflections: 8623 (R(int) = 0.0396); completeness to $\theta = 27.57°$, 99.6%; max./min. transmission: 1.000000/0.550771; data/restraints/parameters: 8623/0/469; goodness-of-fit on F^2: 1.001; final R indices ($I > 2\sigma(I)$): $R1 = 0.0293$, $wR2 = 0.0673$; R indices (all data): $R1 = 0.0323$, $wR2 = 0.0683$; largest diff. peak/hole: 0.957/−0.398 e Å^{-3}. CCDC-677969 (**3**), -677968 (**5**), and -677970 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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