Formation of Fischer Carbene Complexes in Asymmetric Aldol-Type Condensation of an Isocyanide Component on Bis(oxazolinyl)phenylrhodium(III) Complexes with Aldehydes: Stereochemistry, Structural Characterization, and Mechanistic Studies

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The reaction of (Phebox)$RhCl_2(H_2O)$ complexes **3** (Phebox = 2,6-bis(oxazolinyl)phenyl) with methyl isocyanoacetate (**1**) and (*p*-tolylsulfonyl)methyl isocyanide (TosMIC; **2**) provided the corresponding isocyanide complexes (Phebox)$RhCl_2$(L) (**4**, L = methyl isocyanoacetate; **5**, L = TosMIC) in almost quantitative yields. These isocyanide complexes **4** and **5** readily reacted with aldehydes in the presence of *t*-BuOK to give the aldol adducts as diastereomeric mixtures of chiral Fischer carbene complexes **6**−**9**. NMR study and X-ray crystallography of these carbene complexes revealed that (1) the aldol reactions proceed with *trans* stereoselectivity with modest to good diastereofacial selectivities on the (Phebox)$RhCl_2$ fragments, (2) the carbene fragments act as basic σ-donor ligands, and (3) the hybridization of the carbene carbon atoms is sp^2 and the electron-deficient carbene carbon centers are π-conjugated with both neighboring nitrogen and oxygen atoms. We also succeeded in the isolation of both enantiomers of 2-oxazoline derivative **14** from the corresponding chiral carbene complexes **8** by treatment with $AgBF_4$.

Introduction

Ever since Schöllkopf and Gerhart discovered that isocyanides could be anionized (metalated) at the α-position in 1968, isocyanides having acidic hydrogens at the α-carbon atom have been found to be versatile reagents for the nucleophilic introduction of (masked) α-aminoalkyl groups or synthesis of heterocyclic compounds.[1] For asymmetric reactions with isocyanides as substrates using chiral metal complexes, it is necessary to design ligand systems having deep chiral surroundings, because the enantioselective carbon−carbon bond formation is accomplished at the α-carbon atom, very distant from the metal center.

Previously, we have designed an anionic "N−C−N pincer" ligand,[2−6] 2,6-bis(oxazolinyl)phenyl (abbreviated as Phebox),[7,8] and synthesized chiral rhodium(III) aqua complexes as new types of transition-metal Lewis acids[9] (Figure 1; **3**). We have demonstrated that (Phebox)-$RhCl_2$(vacant), generated by releasing H_2O from aqua complexes **3**, captures a carbonyl oxygen to make C=O/σ-type carbonyl complexes and, therefore, acts as a traditional Lewis acid catalyst for the enantioselective allylation of aldehydes[7b,e] and hetero Diels−Alder reaction of Danishefsky's dienes.[7d] During the course of our studies on the Phebox−Rh(III) systems as chiral transition-metal Lewis acids, we have found that isocyanide compounds can bind to the rhodium atom, forming

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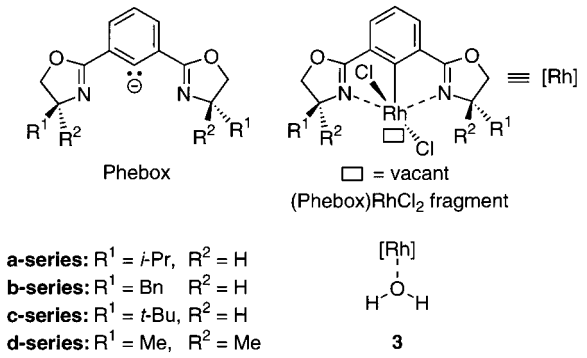
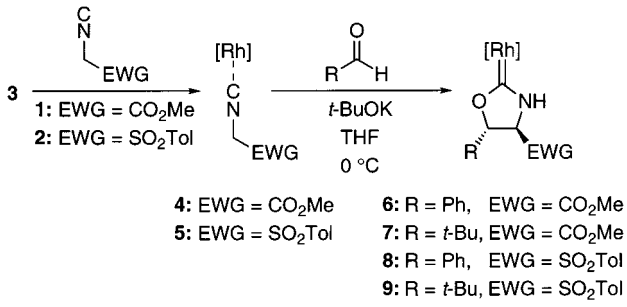


Figure 1.

stable isocyanide complexes; furthermore, these isocyanide components on the (Phebox)$RhCl_2$ fragments readily reacted with aldehydes to afford the corresponding aldol adducts[10] as diastereomeric mixtures of chiral

Scheme 1



Fischer carbene complexes (Scheme 1). To our knowledge, there has been no report on the synthesis and isolation of Fischer carbene complexes in the aldol-type condensation of isocyanides and aldehydes since two independent groups first described the achiral platinum and osumium complexes in 1975.[11] Not only chiral metal isocyanides but also chiral Fischer carbene complexes have been recognized to offer a variety of potential applications in asymmetric synthesis.[12,13] For the creation of new reaction systems and elucidation of reaction mechanisms, it is of importance to study the structural characterization of the chiral Fischer carbene complexes and to clarify the steric course during the asymmetric induction of bound isocyanides in coordination spheres.[14] Herein we disclose chiral Phebox−Rh(III)−isocyanide complexes and their application to asymmetric aldol-

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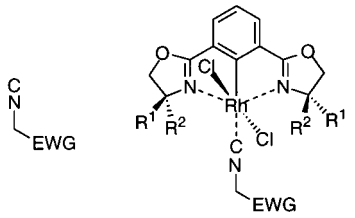
Table 1. Selected Spectroscopic Data for Isocyanide Compounds



1: EWG = CO_2Me **4:** EWG = CO_2Me
2: EWG = SO_2Tol **5:** EWG = SO_2Tol

compd	yield, %	IR[a] ν, cm^{-1} CN	^{1}H NMR[b] δ, ppm (J_{gem}, Hz) H_α	^{13}C NMR[c] δ, ppm (J_{Rh-C}, Hz) CN	C_α
1		2166	4.24 (2H)	161.6	43.4
4a	99	2212	4.73 (2H)	150.6 (34.9)	45.3
4b	99	2207	4.76 (2H)	150.4 (34.9)	45.5
4c	99	2211	4.69 (2H)	153.2 (31.6)	45.4
4d	98	2199	4.82 (2H)	151.2 (35.7)	45.4
2		2150	4.58 (2H)	166.1	61.4
5a	99	2188	4.98, 5.02 (15.4)	154.7 (36.0)	62.7
5b	98	2186	4.98, 5.05 (15.2)	154.2 (36.2)	63.0
5c	99	2194	4.91, 4.97 (15.4)	157.2 (38.3)	62.9

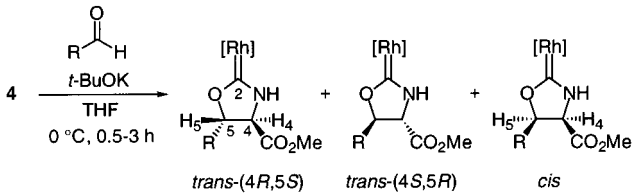
[a] Observed as KBr pellets. [b] Observed at 400 MHz in $CDCl_3$ at room temperature. [c] Observed at 100 MHz in $CDCl_3$ at room temperature.

type condensation with aldehydes in order to study asymmetric induction in a stoichiometric manner. We also describe the structural characterization of the Fischer carbene complexes obtained, mechanistic studies of the reaction pathway, and the transition state assembly on the basis of X-ray crystallography and NMR evidence.

Results and Discussion

1. Synthesis and Structural Studies of (Phebox)-$RhCl_2$(isocyanide) Complexes 4−5. Treatment of aqua complexes **3** with methyl isocyanoacetate (**1**) or (*p*-tolylsulfonyl)methyl isocyanide (TosMIC; **2**) in dichloromethane spontaneously produced the corresponding isocyanide complexes (Phebox)$RhCl_2$(L) (**4**, L = methyl isocyanoacetate; **5**, L = TosMIC) in 98−99% yields as stable pale yellow solids. Table 1 lists some of the relevant spectroscopic data. Although the CN stretching bands of all complexes are observed at the normal range of the CN triple bonds (2186−2212 cm^{-1}), the signals for isocyanide carbons on the (Phebox)$RhCl_2$ fragments appear at higher field (∼12 ppm) than the uncomplexed (free) ones (δ 161.6 ppm for **1** and δ 166.1 ppm for **2**) with ^{103}Rh−^{13}C couplings (31.6−38.3 Hz) on the ^{13}C NMR spectra. Therefore, we concluded that the isocyanides are coordinated to the (Phebox)$RhCl_2$ fragments by the isocyanide's carbons. Because of its potentially diastereotopic environments, the signals for the α-methylene protons (H_α) of bound isocyanides to the chiral (Phebox)$RhCl_2$ fragments can be observed as two nonequivalent AB patterns such as TosMIC complexes **5**. However, ^{1}H NMR spectra for the chiral methyl isocyanoacetate complexes **4a**−**c** show the equivalent CH_2-CO_2Me signals. These results indicated that the rotation along the C_α−$N_{isocyanide}$ bond is faster than the NMR time scale for the methyl isocyanoacetate complexes **4**.

Table 2. Asymmetric Aldol-Type Condensation of Methyl Isocyanoacetate Complexes 4 and Aldehydes[a]



trans-(4*R*,5*S*) *trans*-(4*S*,5*R*) *cis*

6: R = Ph
7: R = *t*-Bu

entry	substrate/ product	4*R*,5*S*	% yield[b] 4*S*,5*R*	% de[b] *cis*	*trans*
1	**4a/6a**	46	35	9	14
2	**4a/7a**	64 (63)[c]	36 (22)[c]	0	28
3	**4b/7b**	91 (48)[c]	9	0	82
4	**4d/7d**	100 (90)[c]		0	

[a] All reactions were carried out using 1 equiv of methyl isocyanoacetate complexes **4**, 1 equiv of *t*-BuOK, and 1.2 equiv of aldehydes in THF at 0 °C. [b] Determined by ^{1}H NMR analysis. [c] Isolated yield.

2. Asymmetric Aldol-Type Condensation of Isocyanide Complexes. (i) Reaction of Methyl Isocyanoacetate Complexes 4. At first, the aldol-type condensation of the *i*-Pr-Phebox-derived methyl isocyanoacetate complex **4a** and benzaldehyde was performed with several bases as deprotonating reagents. However, no reaction occurred by the use of tertiary amines or K_2CO_3. Finally, we found that the present reaction proceeds smoothly in THF at 0 °C by the use of 1 equiv of *t*-BuOK as a base. The ^{1}H NMR spectrum of the crude products indicated the formation of the three aldol adducts **6a** as stereoisomers in 46%, 35%, and 9% yields, respectively (Table 2, entry 1). Two of them exhibited characteristic signals as carbene moieties on the ^{13}C NMR with ^{103}Rh−^{13}C couplings: Rh=$C_{carbene}$ at δ 228.4 ppm (J_{Rh-C} = 31.8 Hz) and δ 228.6 ppm (J_{Rh-C} = 31.4 Hz), respectively (Table 3).[15,16] Therefore, we assumed that these aldol adducts are the oxazolidin-2-ylidene Fischer carbene complexes. This inference is also substantiated by the characteristic N*H* proton signals as broad singlets at δ 9.76−9.77 ppm.[15,16] Usually, *trans* isomers display smaller vicinal (H_4−H_5) coupling constants than do *cis* isomers. Thus, the relative stereochemistry for the carbene fragment of the minor complex (J_{vic} = 11.4 Hz) is thought to be the *cis* configuration, and the others with small (6.8 and 6.4 Hz) coupling constants may be *trans* diastereomers. However, these carbene complexes were unstable and could not be isolated. Next, we carried out the reaction of chiral isocyanide complexes **4a** and **4b** and the nonchiral complex **4d** with pivalaldehyde in a similar

(15) Reviews of the =CXY type carbene complexes: (a) Fehlhammer, W. P.; Fritz, M. *Chem. Rev.* **1993**, *93*, 1243. (b) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725. (c) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162. (d) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. See also ref 12a.

(16) (a) Macomber, D. W.; Rogers, R. D. *J. Organomet. Chem.* **1986**, *308*, 353. (b) Cetinkaya, B.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F. *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1989; pp 59−66. (c) Werner, H.; Hörlin, G.; Mahr, N. *J. Organomet. Chem.* **1998**, *551*, 367. (d) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *Organometallics* **1998**, *17*, 2162.

Table 3. Selected Spectroscopic Data for Carbene Complexes 6 and 7

complex	dec pt, °C	IR[a] ν_{NH}, cm^{-1}	^{1}H NMR[b] δ_{NH}, ppm	^{1}H NMR[b] $\delta_{H4,H5}$, ppm [J_{vic}, Hz]	^{1}H NMR[b] δ_{OMe}, ppm	^{13}C NMR[c] $\delta_{C_{carbene}}$, ppm [J_{Rh-C}, Hz]
(4*R*,5*S*)-**6a**			9.76	4.81, 6.41 [6.8]	3.93	228.4 [31.8]
(4*S*,5*R*)-**6a**			9.77	4.78, 6.32 [6.4]	3.92	228.6 [31.4]
cis−**6a**			9.77	6.45 (H_5) [11.4]	3.86	
(4*R*,5*S*)-**7a**	138	3467	9.53	4.48, 5.09 [7.4]	3.96	227.8 [32.3]
(4*S*,5*R*)-**7a**	148	3471	9.63	4.48, 4.98 [6.8]	3.86	227.6 [32.8]
(4*R*,5*S*)-**7b**	216	3458	9.68	4.53, 5.14 [7.5]	3.35	228.1 [31.3]
(4*S*,5*R*)-**7b**			9.82		3.81	
7d	193	3458	9.78	4.55, 5.12 [8.5]	3.84	228.5 [32.0]

[a] Observed as KBr pellets. [b] Observed at 400 MHz in $CDCl_3$ at room temperature. [c] Observed at 100 MHz in $CDCl_3$ at room temperature.

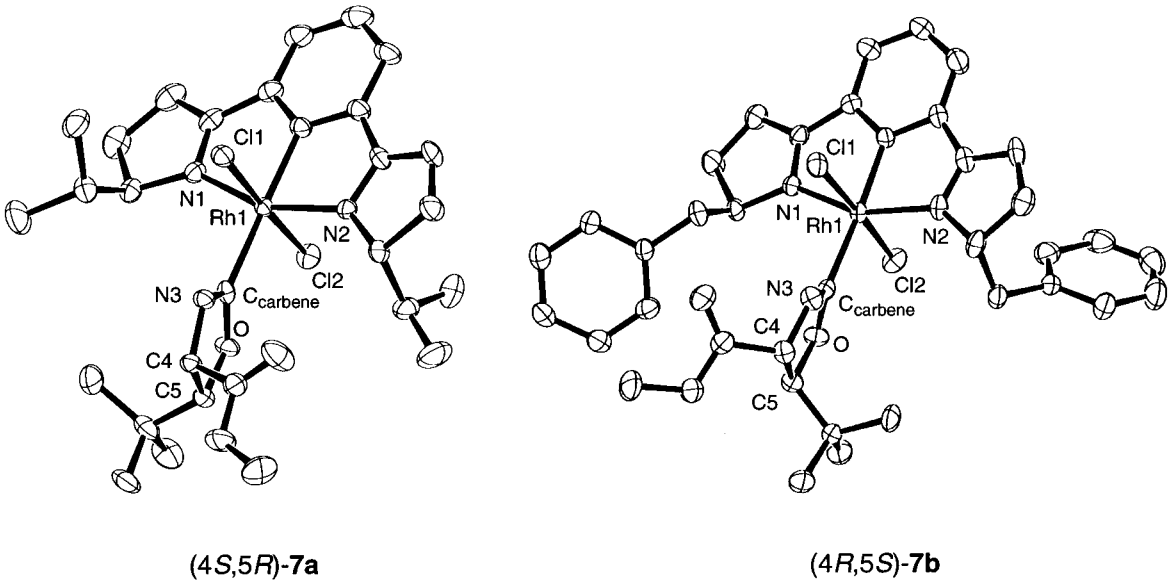
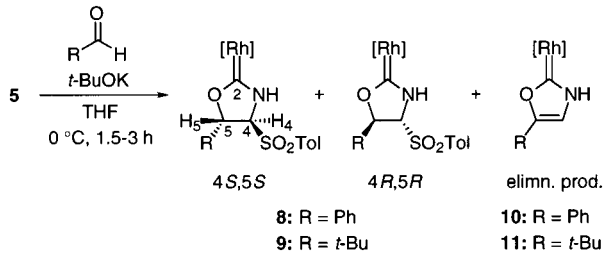


Figure 2. Molecular structures of (4*S*,5*R*)-**7a** (left) and (4*R*,5*S*)-**7b** (right).

manner. In all of the experiments, the reaction proceeded smoothly to afford the corresponding aldol adducts in quantitative yields. The carbene complexes obtained, **7**, are only trans stereoisomers and could be isolated in pure form by silica gel chromatography at 0 °C, except for the Bn-Phebox-derived minor isomer (entries 2−4). These preferencial *trans* diastereoselectivities are not due to the chirality on the Phebox ligand but to the structures of the (Phebox)$RhCl_2$ fragments, since the diastereoselectivity of the reaction with the nonchiral dMe-Phebox-derived **4d** is also *trans* stereospecific. Although the diastereomeric excess of the aldol adducts **7a** is only 28%, the Bn-Phebox-derived compound **4b** shows high diastereofacial selectivity (82% de). With the expectation of increasing diastereofacial selectivity, we also attempted the reaction at lower temperature. However, decomposition of the isocyanide complex **4b** into the aqua complex **3b** was fast, and only a trace amount of the desired carbene complex **7b** was obtained. It is worth noting that all major *trans* isomers, including benzaldehyde-derived **6a**, display more high-field shifts for the N*H* signals and larger vicinal (H_4−H_5) coupling constants than do minor isomers in the ^{1}H NMR spectra. Finally, we succeeded in the structural characterization of the minor and major isomers **7a** and **7b**, respectively, by X-ray diffraction and revealed that the absolute configurations of the carbene moieties on major diastereomers are 4*R*,5*S* based on the chiral (*S*,*S*)-Phebox structures (Figure 2). Structural features will be discussed later.

(ii) Reaction of TosMIC Complexes 5. Next, we examined the aldol-type condensation of the TosMIC complexes **5** with aldehydes in a manner similar to the reaction of methyl isocyanoacetate comolexes. The ^{1}H NMR spectrum of the crude products for the reaction of *i*-Pr-Phebox-derived complex **5a** and benzaldehyde indicated formation of the two carbene complexes **8a** as stereoisomers in quantitative yield. Relative stereochemistries on the carbene moieties are found to be the *trans* configuration for both complexes by the small vicinal coupling constants (J_{H4-H5} = 5.6 and 4.8 Hz, respectively), but the diastereomer ratio is 50:50 (Table 4, entry 1). These diastereomers were separated by silica gel chromatography at 0 °C, and the *trans*-(4*R*,5*R*) structure of one of the diastereomers could be characterized by X-ray diffraction (Figure 3; for a detailed discussion, see below). The relationship between the chemical shifts for the N*H* signals, vicinal (H_4−H_5) coupling constants, and the absolute configurations on the carbene parts for the TosMIC-derived carbene complexes can be assigned in a manner similar to that for the methyl isocyanoacetate derived complexes: the 4*R*,5*R* isomer displays more low-field shifts for the N*H* signals and smaller vicinal (H_4−H_5) coupling constants on the ^{1}H NMR spectra (Table 5). In the reaction of the Bn-Phebox-derived complex **5b** and benzaldehyde, sur-

Table 4. Asymmetric Aldol-Type Condensation of TosMIC Complexes 5 and Aldehydes[a]



entry	substrate/ product	% yield[b] 4*S*,5*S*	4*R*,5*R*	elimin product
1	**5a/8a**	50 (35)[c]	50 (38)[c]	0 (**10a**)
2	**5b/8b**	31	65	0 (**10b**)
3	**5c/8c**	38	24	31 (**10c**)
4	**5a/9a**	40 (31)[c]	29	23 (**11a**)
5	**5b/9b**	26	45	29 (**11b**)

[a] All reactions were carried out using 1 equiv of TosMIC complexes **5**, 1 equiv of *t*-BuOK, and 1.2 equiv of aldehydes in THF at 0 °C. [b] Determined by ^{1}H NMR analysis. [c] Isolated yield.

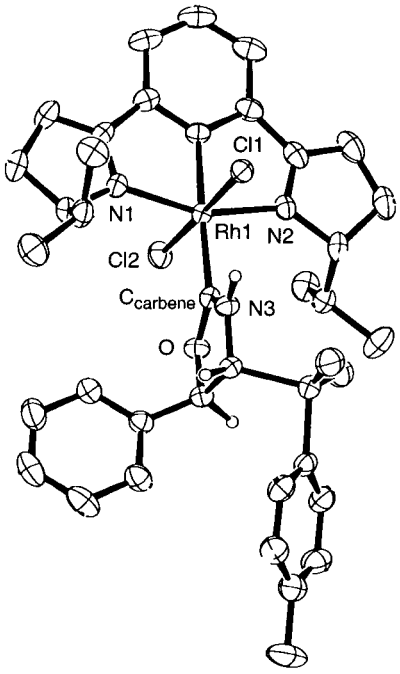


Figure 3. Molecular structure of (4*S*,5*R*)-**8a**. For clarity, only H atoms on the carbene fragment are shown.

prisingly, the opposite *trans* diastereomer (4*R*,5*R*)-**8b** was obtained as the major product with 35% de (entry 2). The reaction of **5c** afforded the oxazol-2-ylidene complex **10c** in 31% yield as a byproduct, which was formed by eliminating *p*-toluenesulfinic acid from the carbene complexes **8c** (entry 3).[17] The similar elimination products **11a** and **11b** were produced in 23−29% yield by reactions with pivalaldehyde, and the absolute configurations on the carbene parts for complexes **9a** and **9b** were of opposite stereochemistry (entries 4 and 5).

3. Structures, Stabilities, and Reactivities of Chiral Fischer Carbene Complexes. (i) Structures of the Carbene Moieties. Two methyl isocyanoacetate derived carbene complexes, (4*S*,5*R*)-**7a** and (4*R*,5*S*)-**7b**, and one TosMIC-derived complex, (4*R*,5*R*)-**8a**, have been characterized by X-ray crystallography (Figures 2 and 3), and the relevant bond distances and angles are summarized in Table 6. The Rh1−$C_{carbene}$ lengths (2.113−2.112 Å) fall in the range observed for similar complexes,[18] and such long Rh1−$C_{carbene}$ distances suggest that these carbene complexes can be described as Lewis acid−base adducts; the carbene fragments act as basic σ-donors. The sums of angles around the carbene carbons for these three complexes are almost 360°, indicating that the hybridization of the $C_{carbene}$ atoms is sp^2. Both the O−$C_{carbene}$ and the N3−$C_{carbene}$ bond distances for these complexes are shorter than the normal ranges of X−C (X = O, N) single bonds. In this geometries, the electron-deficient carbene carbon centers are π-conjugated with two heteroatoms; the mesomeric structure **A** makes a strong contribution (Chart 1). Although the bound carbene planes of (4*S*,5*R*)-**7a** (EWG = CO_2Me) and (4*R*,5*R*)-**8a** (EWG = SO_2Tol) are almost perpendicular to the Phebox planes (θ = 85°), the bound carbene moiety on (4*R*,5*S*)-**7b** leans toward the Phebox plane from the Cl−Rh−Cl plane; the dihedral angle between the carbene part and the Phebox plane is about 70° (Chart 2). This slope of the carbene moiety is due to the steric repulsion between the substituents on the Phebox ligand and both EWG and R groups on the carbene fragment.

Chart 1

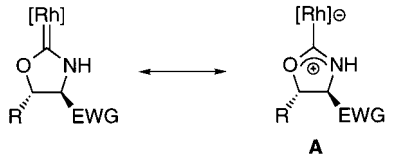
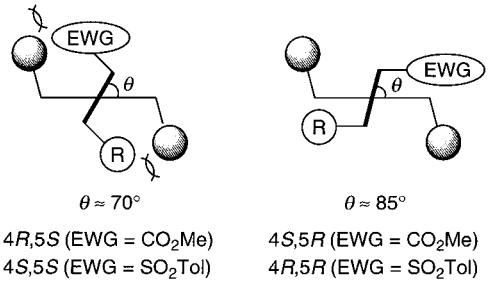


Chart 2



(ii) Stabilities of the Carbene Complexes. To study the differences of the stabilitiy between both diastereomers (4*S*,5*S* and 4*R*,5*R*), we carefully examined the reaction of the *i*-Pr-Phebox-derived TosMIC complex **5a** and benzaldehyde. ^{1}H NMR spectra showed only the desired carbene complexes (4*S*,5*S*)-**8a** and (4*R*,5*R*)-**8a** within 1.5 h in the ratio 50:50. However, these carbene complexes gradually decomposed, and signals due to the oxazol-2-ylidene complex **10a**, which was formed by eliminating HSO_2Tol from the carbene complexes **8a**, appeared after completion of the aldol-type condensation. The amounts of these three complexes were 16% for (4*S*,5*S*)-**8a**, 37% for (4*R*,5*R*)-**8a**, and

(17) van Leusen, A. M.; Hoogenboom, B. E.; Siderius, H. *Tetrahedron Lett.* **1972**, 2369. See also ref 16b.

(18) (a) Beck, W.; Weigand, W.; Nagel, U.; Schaal, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 377. (b) Rieger, D.; Lotz, S. D.; Kernbach, U.; Andre, C.; Bertran-Nadal, J.; Fehlhammer, W. P. *J. Organomet. Chem.* **1995**, *491*, 135. See also refs 14 and 15.

Table 5. Selected Spectroscopic Data for Carbene Complexes 8−11

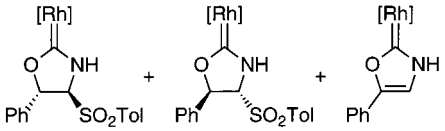
complex	dec pt, °C	IR[a] ν_{NH}, cm^{-1}	^{1}H NMR[b] δ_{NH}, ppm	^{1}H NMR[b] $\delta_{H4,H5}$, ppm [J_{vic}, Hz]	^{1}H NMR[b] δ_{Tol-Me}, ppm	^{13}C NMR[c] $\delta_{C_{carbene}}$, ppm [J_{Rh-C}, Hz]
(4*S*,5*S*)-**8a**	195	3449	9.60	5.03, 6.86 [5.6]	2.46	232.2 [32.0]
(4*R*,5*R*)-**8a**	190	3449	9.94	5.01, 6.79 [4.8]	2.48	232.4 [32.3]
10a			11.77			212.5 [33.8]
(4*S*,5*S*)-**8b**			9.77	5.13 (H_4) [5.8]	2.39	
(4*R*,5*R*)-**8b**			10.05	5.04 (H_4) [4.7]	2.46	
(4*S*,5*S*)-**8c**			9.16	5.09, 6.80 [8.2]	2.50	
(4*R*,5*R*)-**8c**			9.82	4.99, 6.65 [7.9]	2.49	
10c			11.57			
(4*S*,5*S*)-**9a**	174	3455	9.32	4.78, 5.46 [5.9]	2.46	231.6 [31.8]
(4*R*,5*R*)-**9a**			9.79	4.77, 5.47 [5.8]	2.46	
11a			11.42			
(4*S*,5*S*)-**9b**			9.72	4.97, 5.29 [5.9]	2.28	
(4*R*,5*R*)-**9b**			9.84	4.77, 5.51 [4.8]	2.45	
11b			11.68			

[a] Observed as KBr pellets. [b] Observed at 400 MHz in $CDCl_3$ at room temperature. [c] Observed at 100 MHz in $CDCl_3$ at room temperature.

Table 6. Selected Bond Distances (Å) and Angles (deg) for the Carbene Complexes (4*S*,5*R*)-7a, (4*R*,5*S*)-7b, and (4*R*,5*R*)-8a

	(4*S*,5*R*)-**7a**	(4*R*,5*S*)-**7b**	(4*R*,5*R*)-**8a**
Rh1−Cl1	2.346(2)	2.336(2)	2.351(2)
Rh1−Cl2	2.340(2)	2.364(2)	2.340(2)
Rh1−N1	2.074(7)	2.086(6)	2.072(4)
Rh1−N2	2.041(7)	2.057(6)	2.059(4)
Rh1−$C_{carbene}$	2.115(9)	2.122(8)	2.113(5)
O−$C_{carbene}$	1.33(1)	1.324(9)	1.322(6)
N3−$C_{carbene}$	1.33(1)	1.316(9)	1.319(7)
O−C_5	1.49(1)	1.467(9)	1.478(6)
N3−C_4	1.45(1)	1.439(10)	1.449(7)
C_4−C_5	1.54(1)	1.56(1)	1.528(8)
N1−Rh1−N2	157.5(3)	155.9(3)	156.7(2)
Rh1−$C_{carbene}$−O	126.7(6)	125.4(5)	125.1(4)
Rh1−$C_{carbene}$−N3	123.8(7)	125.0(6)	125.2(4)
O−$C_{carbene}$−N3	109.1(8)	109.6(7)	109.7(4)

Chart 3



	(4*S*,5*S*)-**8a**		(4*R*,5*R*)-**8a**		**10a**
< 1.5 h	50	:	50	:	0
2.5 h	16	:	37	:	47

47% for **10a** (Chart 3). This result shows that the decomposition rate of the sterically hindered (4*S*,5*S*)-**8a** is much faster (ca. 2.6 times) than that of the less hindered 4*R*,5*R* isomer. The elimination product **10c** is rearranged to the N-bonded oxazole complex **12** during column purification. The structure of **12** was determined by X-ray diffraction (Figure 4 and Table 7). Although the N-bonded oxazole complex is stable in the solid state, dissociation of bound oxazole is observed in solution and, finally, both the aqua complex **3a** and free oxazole **13** are obtained (Scheme 2).

(iii) Formation of Optically Pure 2-Oxazolines from Carbene Complexes. We also succeeded in the isolation of the optically pure 2-oxazoline derivative **14** from the chiral carbene complexes **8a** by treatment with $AgBF_4$ (Scheme 3). To a solution of (4*S*,5*S*)-**8a** in dichloromethane was added 2.1 equiv of $AgBF_4$ at 20 °C. After it was stirred for 1.5 h at that temperature, the reaction mixture was filtered through a pad of alumina to afford 5-phenyloxazole (**13**) as the main product and optically pure (4*S*,5*S*)-**14** in 7% yield. In the reaction of sterically less hindered (4*R*,5*R*)-**8a**, the rate of carbene decomposition is slower and the chemical yield of (4*R*,5*R*)-**14** increased to 41%. Optical purities for both (4*S*,5*S*)- and (4*R*,5*R*)-**14** were confirmed by chiral HPLC analysis (Daicel CHIRALCEL OD-H).

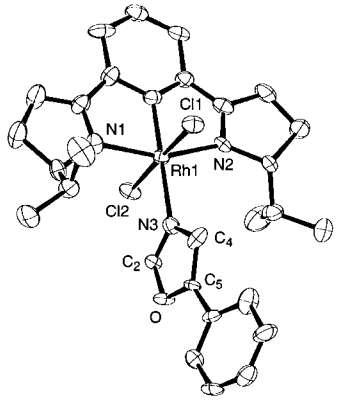


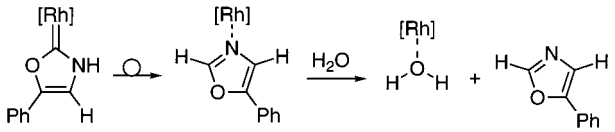
Figure 4. Molecular structure of **12**: one of the two independent crystal structures.

Table 7. Selected Bond Distances (Å) and Angles (deg) for the Oxazole Complex 12[a]

Rh1−Cl1	2.3304(5)	Rh1−Cl2	2.341(4)
Rh1−N1	2.10(1)	Rh1−N2	2.08(1)
Rh1−N3	2.22(2)	N3−C2	1.27(2)
N3−C4	1.44(2)	C4−C5	1.42(2)
N1−Rh1−N2	157.1(5)	Rh1−N3−C2	126(1)
Rh1−N3−C4	128(1)	C3−N3−C5	105(1)

[a] One of the two independentmolecules in the unit cell.

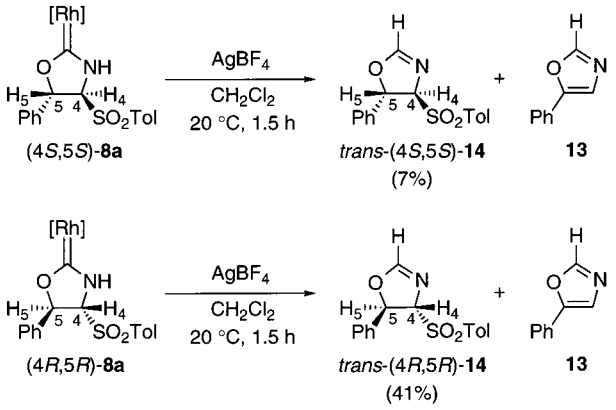
Scheme 2



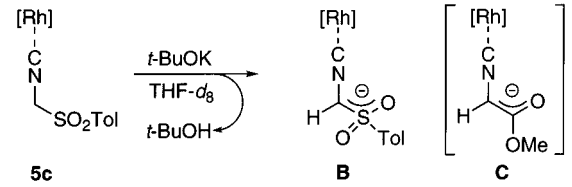
10a **12** **3a** **13**

4. Mechanistic Studies. (i) Reaction Mechanism. It is known that the α-isocyano carbanion species are thermolabile and easily decomposed between −60 and 0 °C.[1] In fact, there is no evidence for the formation of metalated isocyanides bound to the (Phebox)$RhCl_2$ fragments using methyl isocyanoacetate complexes **4**

Scheme 3



Scheme 4



because the decomposition of produced carbanion species is very fast. During careful NMR studies of the reaction of TosMIC complexes **5** with *t*-BuOK, however, we could detect the α-isocyano carbanion species on the ^{1}H NMR (Scheme 4). Deprotonation of the *t*-Bu-Phebox-derived TosMIC complex **5c** with 1 equiv of *t*-BuOK in THF-d_8 was carried out at 0 °C to produce *t*-BuOH (δ 1.14 ppm; s, 9H) and the enolate complex **B**; signals for α-methylene protons disappeared, and the signal assigned to the vinylic proton was observed at δ 7.08 ppm (bs, 1H). Therefore, we assumed that the similar enolate complex **C** is formed by the reaction of methyl isocyanoacetate complexes **4** with *t*-BuOK. This enolate complex **B** is remarkably unstable in solution (THF-d_8) at 20 °C: the decomposition rate was ca. 50% over 1 min. Using other bases such as triethylamine or diisopropylethylamine, no reaction occurred and signals due to only starting isocyanide complexes and tertiary amines were observed. These results imply that the Lewis acidity of (Phebox)$RhCl_2$ fragments is quite low; therefore, strong bases such as *t*-BuOK are needed in order to generate an intermediate isocyano enolate by deprotonation of α-protons.

Usually, this aldol-type condensation proceeds via the mechanism given in Scheme 5.[19] At first, the enolate complex **B** or **C**, generated by deprotonation of isocyanide complexes **4** and **5**, reacts with aldehyde to produce the 2-isocyano alkoxide complex **D**. The cyclization reaction subsequently proceeds to give the metalated oxazoline **E** as an intermediate. Finally the protonation occurs directly at the 2-position on **E**, resulting in the formation of the 2-oxazoline product. Because the aldol adducts are obtained as oxazolidin-2-ylidene type Fischer carbene complexes, final protonation proceeds not at the 2-position but at the N atom

(19) Mechanistic studies using alkali metals: (a) Hoppe, D.; Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 300. (b) Böll, W. A.; Gerhart, F.; Nürrenbach, A.; Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 458. (c) Meyers, A. I.; Collington, E. W. *J. Am. Chem. Soc.* **1970**, *92*, 6676. (d) Schöllkopf, U.; Böhme, P. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 491. See also ref 1b.

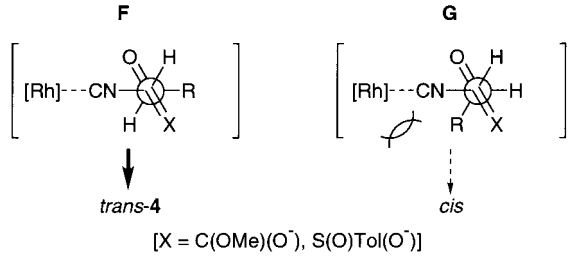
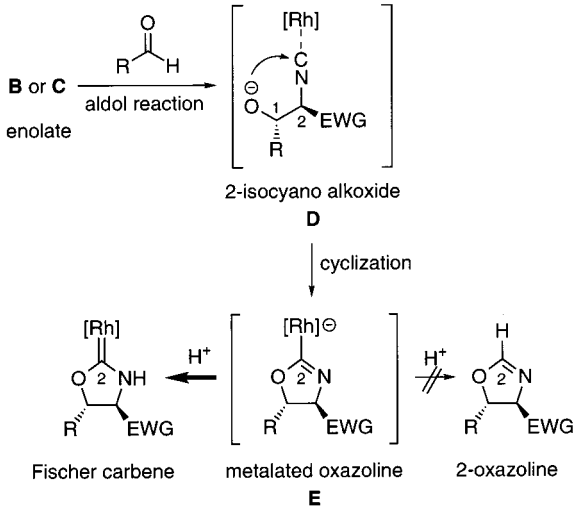


Figure 5. Antiperiplanar transition states **F** and **G**.

Scheme 5

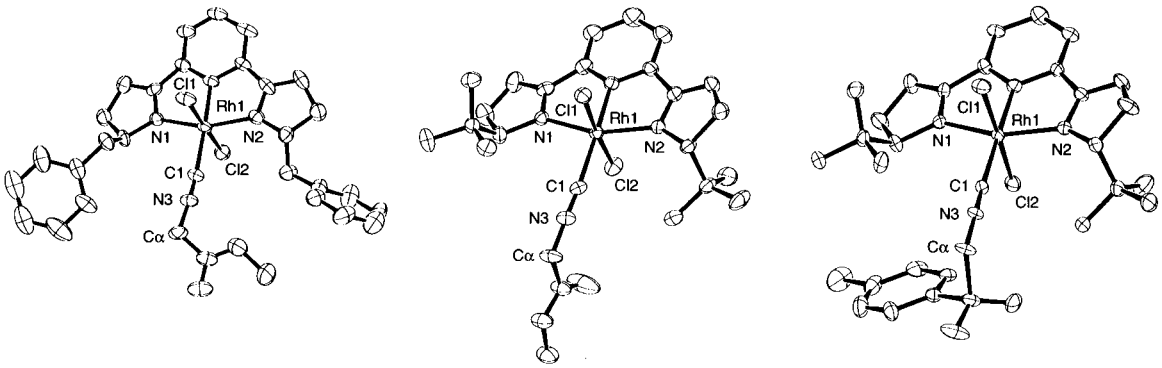


of the metalated oxazoline **E**. However, It is not clear whether the N atom of **E** is protonated via a metal hydride intermediate or direct N protonation occurs.

(ii) Transition State Assembly. Since the relative stereochemistries of carbene complexes **6**−**9** are *trans* configurations, the chiral enolates **B** and **C** react *trans* selectively with aldehydes. This *trans*-selective reaction of the enolates **B** and **C** with aldehydes can be attributed to the *gauche* interaction between the R groups of aldehydes and the isocyano moiety bound to the bulky (Phebox)$RhCl_2$ fragments in antiperiplanar transition states (Figure 5, **F** vs **G**).

The reason the Bn-Phebox-derived complex shows much higher diastereofacial selectivity than do *i*-Pr- or *t*-Bu-Phebox complexes is explained by X-ray analyses of the corresponding isocyanide complexes **4b**,**c** and **5c**. The ORTEP drawings are shown in Figure 6, and selected bond distances and angles are summarized in Table 8. The C_α atoms on the (Phebox)$RhCl_2$ fragments are very distant from the Rh atoms (∼4.68 Å), so that the *i*-Pr or *t*-Bu substituents on the Phebox ligands do not reach out sufficiently to the α-carbon atoms where the diastereofacial selective carbon−carbon bond forms (Figure 6, center and right). The Bn moieties on **4b,** however, make deep chiral surroundings (Figure 6, left); therefore, high diastereofacial selectivity is achieved in the present reaction.

The possible structures of the methyl isocyanoacetate derived enolate complexes **C** are shown in Figure 7. The observed 4*R*,5*S* stereochemistry of the carbene parts using the (*S*,*S*)-(Bn-Phebox)$RhCl_2$ fragment can be unambiguously explained by the intermediate **C′**. The enolate plane bound to the Rh atom is perpendicular to the Phebox plane, and the *si* face of the enolate is



4b **4c** **5c**

Figure 6. Molecular structures of the isocyanide complexes **4b** (left), **4c** (center), and **5c** (right).

Table 8. Selected Bond Distances (Å) and Angles (deg) for the Isocyanide Complexes 4b,c and 5c

	4b	4c	5c[a]
Rh1−Cl1	2.350(3)	2.338(2)	2.339(4)
Rh1−Cl2	2.341(3)	2.356(2)	2.361(3)
Rh1−N1	2.049(8)	2.092(7)	2.082(10)
Rh1−N2	2.063(8)	2.096(7)	2.102(10)
Rh1−C1	2.104(9)	2.122(9)	2.11(1)
N3−C1	1.13(1)	1.14(1)	1.13(2)
N3−Cα	1.44(1)	1.43(1)	1.44(2)
N1−Rh1−N2	157.3(3)	157.8(3)	157.4(4)
Rh1−C1−N3	175(1)	171.9(8)	173(1)
C1−N3−Cα	175(1)	178.8(9)	173(1)

[a] One of the two independent molecules in the unit cell.

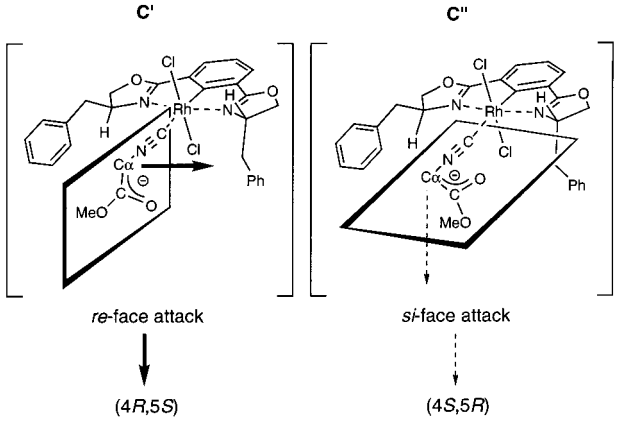


Figure 7. Structures of the enolate complexes **C′** (left) and **C″** (right).

masked by one benzyl substituent on the oxazoline rings. The aldehydes attacked the exposed *re* face of the bound enolate, and so the 4*R*,5*S* product was obtained. If the bound enolate plane was placed almost parallel to the Phebox plane (**C″**), the opposite product, 4*S*,5*R*, would be obtained as the major isomer.

The resulting opposite diastereofacial selection using the Bn-Phebox-derived TosMIC complex **5b** is shown by the intermediate **B″** in Figure 8. When the enolate plane is perpendicular to the Phebox plane, as in the isocyanoacetate complex **C′**, steric repulsion between the bulky tolyl group on the sp^3 sulfur atom and one benzyl substituent on the oxazoline rings occurs (**B′**). Therefore, the enolate plane rotates along the N−C_α bond to avoid this steric repulsion (**B″**). In such a case, the *si* face of the bound enolate plane is shielded by one benzyl substituent on the oxazoline rings.

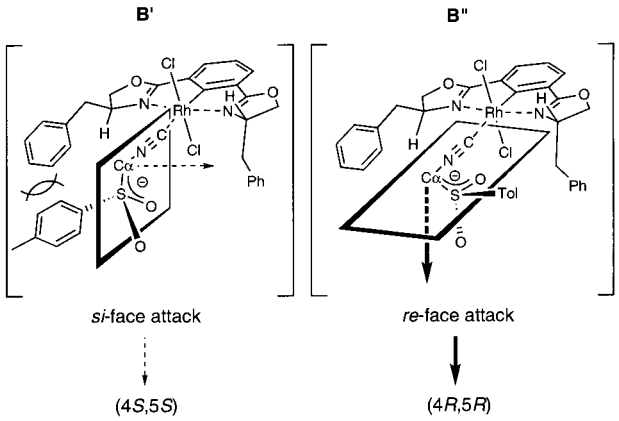


Figure 8. Structures of the enolate complexes **B′** (left) and **B″** (right).

Conclusion

We have synthesized the isocyanide complexes bound to the chiral (Phebox)$RhCl_2$ fragments and succeeded in the structural characterization of these chiral isocyanide complexes by NMR and X-ray studies. We have demonstrated asymmetric aldol-type condensation of isocyanides and aldehydes on the (Phebox)$RhCl_2$ fragments and found that the aldol adducts were obtained as chiral Fischer carbene complexes. NMR and X-ray crystallography revealed that the Bn-Phebox-derived rhodium(III) fragments having deep chiral pockets acted as efficient chiral assemblies[20] for the present reaction, even in a stoichiometric manner. To the best of our knowledge, this is the first example of a full structural characterization of both chiral isocyanides and Fischer carbene complexes in the present aldol-type condensation. We have also succeeded in the isolation of optically pure 2-oxazolines from the corresponding chiral carbene complexes. These findings have provided important information about the steric course of the asymmetric aldol-type condensation of isocyanides and aldehydes by Lewis acid coordination. We will now apply this knowledge to catalytic asymmetric reactions.[21]

(20) Representative papers of chiral assemblies for asymmetric synthesis are as follows. Asymmetric conjugate addition of enones: (a) Wang, Y.; Gladysz, J. A. *J. Org. Chem.* **1995**, *60*, 903. Asymmetric [2,3] rearrangement: (b) Bell, P. T.; Cagle, P. C.; Vichard, D.; Gladysz, J. A. *Organometallics* **1996**, *15*, 4695. Asymmetric Claisen rearrangement: (c) Maruoka, K.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1995**, *117*, 1165. Asymmetric alkylation of aldehydes: (d) Saito, S.; Kano, T.; Hatanaka, K.; Yamamoto, H. *J. Org. Chem.* **1997**, *62*, 5651. Asymmetric oxidation of sulfides: (e) Schenk, W. A.; Frosch, J.; Adam, W.; Prechtl, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1609.

Experimental Section

General Methods. Anhydrous dichloromethane and tetrahydrofuran were purchased from Kanto Chemical Co. (*p*-Tolylsulfonyl)methyl isocyanide (TosMIC) and *t*-BuOK were purchased from Tokyo Chemical Industry Co., Ltd. Methyl isocyanoacetate and silver tetrafluoroborate were purchased from Aldrich Chemical Co. ^{1}H and ^{13}C NMR spectra were measured on a Varian Inova-400 (400 MHz) spectrometer. ^{1}H NMR chemical shifts are given in parts per million downfield from tetramethylsilane as an internal standard (δ 0) in $CDCl_3$, unless otherwise noted. ^{13}C NMR chemical shifts are given in parts per million in $CDCl_3$ as an internal standard (δ 77.1), unless otherwise noted. IR spectra were measured on a JASCO FT/IR-230 spectrometer. Melting points were measured on a Yanaco MP-J3 apparatus. Elemental analyses were measured on a Yanaco CHN CORDER MT-6. Column chromatography was performed with silica gel (Merck, Art 7734) and with Al_2O_3 (Merck, Art 1097). Analytical thin-layer chromatography (TLC) was performed on glass plates and aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F_{254}, layer thicknesses 0.25 and 0.2 mm, respectively). Visualization was accomplished by UV light (254 nm), anisaldehyde, and phosphomolybdic acid. All reactions were carried out under a nitrogen or argon atmosphere. (Phebox)$RhCl_2(H_2O)$ complexes (**3a**−**c**) were prepared by our method.[7e]

Synthesis of (dMe-Phebox)$SnMe_3$ and (dMe-Phebox)-$RhCl_2(H_2O)$ (3d). These compounds were prepared from 2-amino-2-methylpropan-1-ol according to our methods.[7e]

(dMe-Phebox)$SnMe_3$: white solids; Mp: 115−118 °C. IR (KBr): ν 2980, 2905, 1647, 1465, 1355, 1295, 1115, 1060, 975 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.23 (s, satellite J_{Sn-H} = 55.6, 53.2 Hz, 9H), 1.39 (s, 12H), 4.09 (s, 4H), 7.34 (t, J = 7.7 Hz, satellite J_{Sn-H} = 7.7 Hz, 1H), 7.94 (d, J = 7.7 Hz, satellite J_{Sn-H} = 11.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.2 (satellite J_{Sn-C} = 384.6, 367.5 Hz), 28.7, 68.1, 79.4, 127.9 (satellite J_{Sn-C} = 8.4 Hz), 131.4 (satellite J_{Sn-C} = 31.7 Hz), 136.3 (satellite J_{Sn-C} = 18.3 Hz), 146.3 (satellite J_{Sn-C} = 455.8, 435.6 Hz), 163.8 (satellite J_{Sn-C} = 15.2 Hz). Anal. Found for $C_{19}H_{28}N_2O_2Sn$: C, 52.63; H, 6.63; N, 6.35. Calcd: C, 52.45; H, 6.49; N, 6.44.

(dMe-Phebox)$RhCl_2(H_2O)$ (3d): pale yellow solids; Mp: >300 °C dec. IR (KBr): ν 3384, 1620, 1487, 1402, 959, 743 cm^{-1}. ^{1}H NMR (400 MHz, THF-d_8): δ 1.47 (s, 12H), 2.66 (bs, 2H), 4.53 (s, 4H), 7.18 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, THF-d_8): δ 27.6, 66.6, 83.2, 122.4, 127.0, 133.2, 169.9 (J_{Rh-C} = 4.2 Hz), 185.4 (J_{Rh-C} = 18.0 Hz). Anal. Found for $C_{16}H_{21}N_2O_3Cl_2Rh$: C, 41.58; H, 4.67; N, 5.89. Calcd: C, 41.49; H, 4.57; N, 6.05%.

Synthesis of (Phebox)$RhCl_2$(isocyanide) Complexes. General Procedure for the Preparation of Isocyanide Complexes. To a stirred solution of aqua complex **3** (1 equiv) in dichloromethane was added isocyanide (1.1 equiv) at room temperature under an argon atmosphere. After it was stirred for 5 min, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in dichloromethane, and then hexane was added to the solution. The resultant precipitate was isolated by filtration, washed with hexane, and dried in vacuo to afford the isocyanide complexes in quantitative yield as pale yellow powders.

(*i*-Pr-Phebox)$RhCl_2(CNCH_2CO_2Me)$ (4a). Mp: 158−159 °C dec. IR (KBr): ν 2957, 2212, 1763, 1619, 1593, 1486, 1399, 1216, 961, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (d, J = 6.4 Hz, 6H), 0.99 (d, J = 7.2 Hz, 6H), 2.47 (qqd, J = 7.2, 6.4, 3.2 Hz, 2H), 3.89 (s, 3H), 4.22 (ddd, J = 10.0, 7.2, 3.2 Hz, 2H), 4.66 (dd, J = 8.8, 7.2 Hz, 2H), 4.73 (s, 2H), 4.74 (dd, J = 10.0, 8.8 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.2, 19.5, 29.5, 45.3, 53.7, 68.0, 71.1, 123.7, 128.0, 130.8, 150.6 (J_{Rh-C} = 34.9 Hz), 163.6, 173.3 (J_{Rh-C} = 3.0 Hz), 193.5 (J_{Rh-C} = 16.3 Hz). Anal. Found for $C_{22}H_{28}N_3O_4Cl_2Rh$: C, 44.16; H, 5.08; N, 7.31. Calcd: C, 46.17; H, 4.93; N, 7.34.

(Bn-Phebox)$RhCl_2(CNCH_2CO_2Me)$ (4b). Single crystals for the X-ray diffraction study were obtained from ethyl acetate−ether−hexane at room temperature. Mp: 117 °C dec. IR (KBr): ν 2939, 2207, 1757, 1618, 1486, 1399, 1220, 969, 741 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.78 (dd, J = 14.4, 11.0 Hz, 2H), 3.70 (s, 3H), 3.79 (dd, J = 14.4, 3.7 Hz, 2H), 4.53 (dd, J = 8.1, 7.9 Hz, 2H), 4.63 (dddd, J = 11.0, 9.2, 7.9, 3.7 Hz, 2H), 4.72 (dd, J = 9.2, 8.1 Hz, 2H), 4.76 (s, 2H), 7.25−7.36 (m, 11H), 7.66 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.6, 45.5, 53.8, 64.1, 75.4, 123.9, 127.0, 128.4, 129.0, 129.1, 130.8, 137.0, 150.4 (J_{Rh-C} = 34.9 Hz), 163.4, 173.8 (J_{Rh-C} = 3.0 Hz), 193.6 (J_{Rh-C} = 15.9 Hz). Anal. Found for $C_{30}H_{28}N_3O_4Cl_2Rh$: C, 53.87; H, 4.22; N, 6.25. Calcd: C, 53.91; H, 4.22; N, 6.29.

(*t*-Bu-Phebox)$RhCl_2(CNCH_2CO_2Me)$ (4c). Single crystals for the X-ray diffraction study were obtained from chloroform−hexane at room temperature. Mp: 112−113 °C dec. IR (KBr): ν 2961, 2211, 1759, 1618, 1485, 1398, 1217, 971, 740 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (s, 18H), 3.84 (dd, J = 9.7, 4.0 Hz, 2H), 4.690 (s, 2H), 4.692 (dd, J = 9.7, 9.2 Hz, 2H), 4.79 (dd, J = 9.2, 4.0 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.62 (d, J = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.3, 35.4, 45.4, 53.7, 72.3, 73.5, 123.6, 128.3, 130.5, 153.2 (J_{Rh-C} = 31.6 Hz), 163.5, 174.6 (J_{Rh-C} = 3.0 Hz), 191.3 (J_{Rh-C} = 15.2 Hz). Anal. Found for $C_{24}H_{32}N_3O_4Cl_2Rh$: C, 48.03; H, 5.31; N, 7.04. Calcd: C, 48.02; H, 5.37; N, 7.00.

(dMe-Phebox)$RhCl_2(CNCH_2CO_2Me)$ (4d). Mp: 203 °C dec. IR (KBr): ν 2929, 2199, 1753, 1618, 1496, 1398, 1228, 962, 758 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55 (s, 12H), 3.92 (s, 3H), 4.54 (s, 4H), 4.82 (s, 2H), 7.28 (t, J = 7.7 Hz, 1H), 7.61 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.8, 45.4, 53.8, 65.8, 81.9, 123.6, 127.9, 131.4, 151.2 (J_{Rh-C} = 35.7 Hz), 163.6, 171.7 (J_{Rh-C} = 3.4 Hz), 193.6 (J_{Rh-C} = 16.0 Hz). Anal. Found for $C_{20}H_{24}N_3O_4Cl_2Rh$: C, 44.04; H, 4.36; N, 7.83. Calcd: C, 44.14; H, 4.44; N, 7.72.

(*i*-Pr-Phebox)$RhCl_2(CNCH_2SO_2p$-Tol) (5a). Mp: 132−134 °C dec. IR (KBr): ν 2959, 2188, 1620, 1594, 1486, 1401, 1337, 1153, 961, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (d, J = 6.8 Hz, 6H), 0.89 (d, J = 7.2 Hz, 6H), 2.25 (qqd, J = 7.2, 6.8, 3.2 Hz, 2H), 2.46 (s, 3H), 4.10 (ddd, J = 10.0, 7.2, 3.2 Hz, 2H), 4.63 (dd, J = 8.8, 7.2 Hz, 2H), 4.72 (dd, J = 10.0, 8.8 Hz, 2H), 4.98 (d, J = 15.4 Hz, 1H), 5.02 (d, J = 15.4 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 8.12 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.2, 19.4, 21.9, 29.6, 62.7, 68.0, 71.2, 123.8, 128.1, 130.0, 130.6, 130.7, 130.8, 132.3, 146.9, 154.7 (J_{Rh-C} = 36.0 Hz), 173.4, 173.3 (J_{Rh-C} = 3.0 Hz), 193.1 (J_{Rh-C} = 16.3 Hz). Anal. Found for $C_{27}H_{32}N_3O_4Cl_2SRh$: C, 48.50; H, 4.86; N, 6.38. Calcd: C, 48.51; H, 4.83; N, 6.29.

(Bn-Phebox)$RhCl_2(CNCH_2SO_2p$-Tol) (5b). Mp: 142 °C dec. IR (KBr): ν 2924, 2186, 1619, 1594, 1487, 1401, 1340, 1153, 970, 741 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18 (s, 3H), 2.66 (dd, J = 14.0, 11.2 Hz, 2H), 3.46 (dd, J = 14.0, 3.6 Hz, 2H), 4.47 (dddd, J = 11.2, 9.2, 7.2, 3.6 Hz, 2H), 4.54 (dd, J = 8.8, 7.2 Hz, 2H), 4.68 (dd, J = 9.2, 8.8 Hz, 2H), 4.98 (d, J = 15.2 Hz, 1H), 5.05 (d, J = 15.2 Hz, 1H), 7.12 (d, J = 8.4 Hz, 2H), 7.22−7.38 (m, 11H), 7.67 (d, J = 7.6 Hz, 2H), 8.12 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 40.8, 62.8, 64.3, 75.4, 124.1, 127.0, 128.5, 129.0, 129.1, 130.0, 130.68,

(21) Representative papers are as follows. Au(I) complexes: (a) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405. (b) Ito, Y.; Sawamura, M.; Hayashi, T. *Tetrahedron Lett.* **1987**, *28*, 6215. (c) Hayashi, T.; Sawamura, M.; Ito, Y. *Tetrahedron* **1992**, *48*, 1999. (d) Pastor, S. D.; Togni, A. *J. Am. Chem. Soc.* **1989**, *111*, 2333. (e) Togni, A.; Pastor, S. D.; Rihs, G. *J. Organomet. Chem.* **1990**, *381*, C21. (f) Pastor, S. D.; Togni, A. *Helv. Chim. Acta* **1991**, *74*, 905. Ag(I) complexes: (g) Sawamura, M.; Hamashima, H.; Ito, Y. *J. Org. Chem.* **1990**, *55*, 5935. Pd(II) and Pt(II) complexes: (h) Gorla, F.; Togni, A.; Venanzi, M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607. (i) Longmire, J. M.; Zhang, X.; Shang, M. *Organometallics* **1998**, *17*, 4374.

130.74, 132.0, 136.7, 147.2, 154.2 (J_{Rh-C} = 36.2 Hz), 173.8 (J_{Rh-C} = 3.4 Hz), 193.4 (J_{Rh-C} = 16.4 Hz). Anal. Found for $C_{35}H_{32}N_3O_4Cl_2SRh$: C, 54.88; H, 4.36; N, 5.46. Calcd: C, 54.99; H, 4.22; N, 5.50.

(*t*-Bu-Phebox)RhCl$_2$(CNCH$_2$SO$_2$*p*-Tol) (5c). Single crystals for the X-ray difflaction study were obtained from ethyl acetate−dichloromethane−hexane at room temperature. Mp: 198 °C dec. IR (KBr): ν 2957, 2194, 1619, 1487, 1397, 1369, 1341, 1153, 972 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (s, 18H), 2.45 (s, 3H), 3.60 (dd, J = 10.0, 4.0 Hz, 2H), 4.67 (dd, J = 10.0, 8.8 Hz, 2H), 4.77 (dd, J = 8.8, 4.0 Hz, 2H), 4.91 (d, J = 15.4 Hz, 1H), 4.97 (d, J = 15.4 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 8.14 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 26.2, 35.3, 62.9, 72.3, 73.5, 123.8, 128.4, 130.4 (2C), 130.9, 132.0, 146.7, 157.2 (J_{Rh-C} = 38.3 Hz), 174.6 (J_{Rh-C} = 3.0 Hz), 191.2 (J_{Rh-C} = 15.2 Hz). Anal. Found for $C_{29}H_{36}N_3O_4Cl_2SRh$: C, 49.85; H, 5.25; N, 5.98. Calcd: C, 50.01; H, 5.21; N, 6.03.

General Procedure for the Aldol-Type Condensation of Isocyanide Complexes and Aldehydes. To a stirred solution of the isocyanide complex (1 equiv) and potassium *tert*-butoxide (1 equiv) in tetrahydrofuran was added aldehyde (1.2 equiv) at 0 °C under an argon atmosphere. After it was stirred for 0.5−3 h at that temperature, the reaction mixture was poured into water at 0 °C, and then the mixture was extracted with ether. The extract was dried over Na_2SO_4 and evaporated under reduced pressure. This crude product was measured by NMR.

Reaction of 4a with Benzaldehyde. (*i*-Pr-Phebox)-RhCl$_2$(=COCH(Ph)CH(CO$_2$Me)NH) (6a). (4*R*,5*S*)-6a. This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78 (d, J = 7.1 Hz, 6H), 0.83 (d, J = 7.0 Hz, 6H), 2.05 (ddd, J = 7.1, 7.0, 3.3 Hz, 2H), 3.93 (s, 3H), 4.00 (ddd, J = 10.1, 7.3, 3.3 Hz, 2H), 4.59 (dd, J = 8.8, 7.3 Hz, 2H), 4.67 (dd, J = 10.1, 8.8 Hz, 2H), 4.81 (d, J = 6.8 Hz, 1H), 6.41 (d, J = 6.8 Hz, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.41−7.56 (m, 5H), 7.63 (d, J = 7.7 Hz, 2H), 9.76 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 19.5, 29.2, 53.7, 64.9, 67.8, 70.7, 89.2, 123.3, 126.0, 127.7, 129.2, 129.5, 131.2, 137.4, 168.6, 174.1 (J_{Rh-C} = 3.2 Hz), 197.1 (J_{Rh-C} = 14.2 Hz), 228.4 (J_{Rh-C} = 31.8 Hz).

(4*S*,5*R*)-6a. This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (d, J = 7.0 Hz, 12H), 2.00 (dsept, J = 3.1, 7.0 Hz, 2H), 3.92 (s, 3H), 4.07 (ddd, J = 10.1, 6.6, 3.1 Hz, 2H), 4.62 (dd, J = 8.8, 6.6 Hz, 2H), 4.71 (dd, J = 10.1, 8.8 Hz, 2H), 4.78 (d, J = 6.4 Hz, 1H), 6.32 (d, J = 6.4 Hz, 1H), 7.28 (t, J = 7.7 Hz, 1H), 7.41−7.56 (m, 5H), 7.63 (d, J = 7.7 Hz, 2H), 9.77 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 19.3, 29.5, 53.7, 64.9, 67.6, 70.9, 89.4, 123.3, 125.9, 127.7, 129.3, 129.6, 131.1, 137.6, 169.1, 174.0 (J_{Rh-C} = 2.8 Hz), 197.0 (J_{Rh-C} = 14.6 Hz), 228.6 (J_{Rh-C} = 31.4 Hz).

***cis*-6a.** This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H; O*Me*), 6.45 (d, J = 11.4 Hz, 1H; H_5), 9.77 (bs, 1H; N*H*).

Reaction of 4a with Pivalaldehyde. (*i*-Pr-Phebox)-RhCl$_2$(=COCH(*t*-Bu)CH(CO$_2$Me)NH) (7a). (4*R*,5*S*)-7a. The product was purified by silica gel chromatography (2:1 hexane−ethyl acetate) at 0 °C in 63% yield. Mp: 138 °C dec. IR (KBr): ν 3467, 2958, 1748, 1618, 1485, 1392, 1216, 1146, 961 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80 (d, J = 6.6 Hz, 6H), 0.84 (d, J = 7.1 Hz, 6H), 1.15 (s, 9H), 2.07 (qqd, J = 7.1, 6.6, 2.9 Hz, 2H), 3.96 (s, 3H), 3.99 (ddd, J = 9.6, 6.6, 2.9 Hz), 4.48 (d, J = 7.4 Hz, 1H), 4.60 (dd, J = 8.8, 6.6 Hz, 2H), 4.65 (dd, J = 9.6, 8.8 Hz, 2H), 5.09 (d, J = 7.4 Hz, 1H), 7.26 (t, J = 7.7 Hz, 1H), 7.61 (d, J = 7.7 Hz, 2H), 9.53 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 19.5, 27.9, 29.1, 34.4, 53.5, 58.6, 67.7, 70.7, 96.6, 123.2, 127.6, 131.1, 169.3, 173.9 (J_{Rh-C} = 2.7 Hz), 197.4 (J_{Rh-C} = 14.7 Hz), 227.8 (J_{Rh-C} = 32.3 Hz). Anal. Found for $C_{27}H_{38}Cl_2N_3O_5Rh$: C, 49.27; H, 5.89; N, 6.31%; Calcd 49.25; H, 5.82; N, 6.38.

(4*S*,5*R*)-7a. The product was purified by silica gel chromatography (2:1 hexane−ethyl acetate) at 0 °C in 22% yield. Single crystals for the X-ray diffraction study were obtained from dichloromethane−ethyl acetate−ether at room temperature. Mp: 148 °C dec. IR (KBr): ν 3471, 2959, 1747, 1618, 1485, 1389, 1221, 1148, 957 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80 (d, J = 7.0 Hz, 6H), 0.82 (d, J = 6.8 Hz, 6H), 1.15 (s, 9H), 1.96 (qqd, J = 7.0, 6.8, 2.9 Hz, 2H), 3.86 (s, 3H), 3.99 (ddd, J = 9.3, 6.4, 2.9 Hz), 4.48 (d, J = 6.8 Hz, 1H), 4.62 (dd, J = 9.0, 6.4 Hz, 2H), 4.69 (dd, J = 9.3, 9.0 Hz, 2H), 4.98 (d, J = 6.8 Hz, 1H), 7.26 (t, J = 7.7 Hz, 1H), 7.61 (d, J = 7.7 Hz, 2H), 9.63 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.8, 19.2, 25.0, 29.3, 34.6, 53.5, 58.4, 67.7, 70.8, 96.9, 123.2, 127.6, 131.1, 170.0, 173.9 (J_{Rh-C} = 2.8 Hz), 197.4 (J_{Rh-C} = 14.6 Hz), 227.6 (J_{Rh-C} = 32.8 Hz). Anal. Found for $C_{27}H_{38}Cl_2N_3O_5Rh$: C, 49.26; H, 5.87; N, 6.32. Calcd: C, 49.25; H, 5.82; N, 6.38.

Reaction of 4b with Pivalaldehyde. (Bn-Phebox)-RhCl$_2$(=COCH(*t*-Bu)CH(CO$_2$Me)NH) (7b). (4*R*,5*S*)-7b. The product was purified by silica gel chromatography (2:1 hexane−ethyl acetate) at 0 °C in 48% yield. Single crystals for the X-ray diffraction study were obtained from dichloromethane−ethyl acetate−ether−hexane at room temperature. Mp: 216 °C dec. IR (KBr): ν 3458, 1617, 1486, 1398, 1219, 1150, 970, 740 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (s, 9H), 2.62 (dd, J = 14.7, 11.2 Hz, 2H), 3.32 (dd, J = 14.7, 3.1 Hz, 2H), 3.35 (s, 3H), 4.40 (dddd, J = 11.2, 8.6, 6.4, 3.1 Hz, 2H), 4.45 (dd, J = 8.4, 6.4 Hz, 2H), 4.53 (d, J = 7.5 Hz, 1H), 4.63 (dd, J = 8.6, 8.4 Hz, 2H), 5.14 (d, J = 7.5 Hz, 1H), 7.11 (d, J = 7.1 Hz, 4H), 7.21−7.32 (m, 7H), 7.66 (d, J = 7.7 Hz, 2H), 9.68 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.0, 34.5, 40.4, 53.3, 58.9, 63.6, 75.0, 97.0, 123.4, 126.8, 127.9, 128.9, 129.0, 131.2, 136.9, 169.1, 174.5 (J_{Rh-C} = 2.7 Hz), 197.5 (J_{Rh-C} = 14.9 Hz), 228.1 (J_{Rh-C} = 31.3 Hz). Anal. Found for $C_{35}H_{38}N_3O_5Cl_2Rh$: C, 55.69; H, 5.14; N, 5.66. Calcd: C, 55.72; H, 5.08; N, 5.57.

(4*S*,5*R*)-7b. This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 (s, 9H), 2.78 (dd, J = 14.1, 10.5 Hz, 2H), 3.63 (dd, J = 14.1, 3.9 Hz, 2H), 3.81 (s, 3H), 4.35−5.03 (m, 8H), 7.02−7.41 (m, 11H), 7.62 (d, J = 7.7 Hz, 2H), 9.82 (bs, 1H).

Reaction of 4d with Pivalaldehyde. (dMe-Phebox)-RhCl$_2$(=COCH(*t*-Bu)CH(CO$_2$Me)NH) (7d). The product was purified by silica gel chromatography (4:1 dichloromethane−ethyl acetate) at 0 °C in 90% yield. Mp: 193 °C dec. IR (KBr): ν 3458, 1617, 1486, 1397, 1219, 1150, 970, 740 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (s, 9H), 1.31 (s, 6H), 1.33 (s, 6H), 3.84 (s, 3H), 4.41 (d, J = 8.2 Hz, 2H), 4.47 (d, J = 8.2 Hz, 2H), 4.55 (d, J = 8.5 Hz, 1H), 5.12 (d, J = 8.5 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.61 (d, J = 7.5 Hz, 2H), 9.78 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.4, 27.3, 27.8, 34.3, 53.3, 58.9, 66.1, 81.9, 97.2, 123.0, 127.4, 131.7, 169.4, 172.3 (J_{Rh-C} = 3.2 Hz), 196.8 (J_{Rh-C} = 15.0 Hz), 228.5 (J_{Rh-C} = 32.0 Hz). Anal. Found for $C_{25}H_{34}N_3O_5Cl_2Rh$: C, 47.70; H, 5.47; N, 6.62. Calcd: C, 47.63; H, 5.44; N, 6.67.

Reaction of 5a with Benzaldehyde. (*i*-Pr-Phebox)-RhCl$_2$(=COCH(Ph)CH(SO$_2$-*p*-Tol)NH) (8a). (4*S*,5*S*)-8a. The product was purified by silica gel chromatography (5:1 hexane−ethyl acetate) at 0 °C in 35% yield. Mp: 195 °C dec. IR (KBr): ν 2959, 1618, 1596, 1479, 1394, 1149, 962 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.75 (d, J = 7.2 Hz, 6H), 0.85 (d, J = 6.8 Hz, 6H), 2.11 (qqd, J = 7.2, 6.8, 3.2 Hz, 2H), 2.46 (s, 3H), 3.96 (ddd, J = 10.0, 7.2, 3.2 Hz, 2H), 4.60 (dd, J = 8.8, 7.2 Hz, 2H), 4.64 (dd, J = 10.0, 8.8 Hz, 2H), 5.03 (d, J = 5.6 Hz, 1H), 6.86 (d, J = 5.6 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.39−7.48 (m, 3H), 7.45 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 9.60 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 19.5, 22.0, 29.1, 67.6, 70.7, 81.4, 87.2, 123.4, 125.4, 127.7, 129.3, 129.5 (2C), 131.1 (2C), 131.9, 136.2, 147.2, 173.9 (J_{Rh-C} = 2.7 Hz),

196.5 (J_{Rh-C} = 14.7 Hz), 232.3 (J_{Rh-C} = 32.0 Hz). Anal. Found for $C_{34}H_{38}N_3O_5Cl_2SRh$: C, 52.62; H, 5.04; N, 5.53. Calcd: C, 52.72; H, 4.94; N, 5.43.

(4*R*,5*R*)-8a. The product was purified by silica gel chromatography (5:1 hexane-ethyl acetate) at 0 °C in 38% yield. Single crystals for the X-ray diffraction study were obtained from ethyl acetate−ether−hexane at room temperature. Mp: 190 °C dec. IR (KBr): ν 3449, 2956, 1618, 1596, 1486, 1387, 1149, 963 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78 (d, J = 6.8 Hz, 6H), 0.86 (d, J = 7.2 Hz, 6H), 2.08 (qqd, J = 7.2, 6.8, 3.2 Hz, 2H), 2.48 (s, 3H), 4.11 (ddd, J = 10.0, 6.4, 3.2 Hz, 2H), 4.64 (dd, J = 8.8, 6.4 Hz, 2H), 4.73 (dd, J = 10.0, 8.8 Hz, 2H), 5.01 (d, J = 4.8 Hz, 1H), 6.79 (d, J = 4.8 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.35−7.45 (m, 5H), 7.47 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 9.94 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.8, 19.3, 22.0, 29.4, 68.1, 70.9, 81.4, 87.5, 123.4, 125.3, 127.7, 129.3, 129.4, 129.7, 131.0, 131.1, 132.1, 136.3, 147.2, 174.0 (J_{Rh-C} = 2.7 Hz), 196.3 (J_{Rh-C} = 14.6 Hz), 232.4 (J_{Rh-C} = 32.3 Hz). Anal. Found for $C_{34}H_{38}N_3O_5Cl_2SRh$: C, 52.79; H, 4.97; N, 5.34. Calcd: C, 52.72; H, 4.94; N, 5.43.

(*i*-Pr-Phebox)RhCl$_2$(=COCH(Ph)CHNH) (10a). This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.72 (d, J = 7.3 Hz, 6H), 0.81 (d, J = 6.8 Hz, 6H), 1.69 (qqd, J = 7.3, 6.8, 3.2 Hz, 2H), 3.95 (ddd, J = 10.1, 7.5, 3.2 Hz, 2H), 4.57 (dd, J = 8.8, 7.5 Hz, 2H), 4.68 (dd, J = 10.1, 8.8 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.40−7.60 (m, 4H), 7.65 (d, J = 7.6 Hz, 2H), 7.89 (d, J = 7.2 Hz, 2H), 11.77 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1 (J_{Rh-C} = 15.0 Hz; C_{ipso}), 212.5 (J_{Rh-C} = 33.8 Hz; $C_{carbene}$).

(*i*-Pr-Phebox)RhCl$_2$(5-phenyloxazole) (12). The product was purified by silica gel chromatography (5:1 hexane-ethyl acetate) at 0 °C in 12% yield. Single crystals for the X-ray diffraction study were obtained from toluene−hexane at room temperature. Mp: 202 °C dec. IR (KBr): ν 2958, 1620, 1485, 1395, 1333, 1147, 966 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.73 (d, J = 7.1 Hz, 6H), 0.83 (d, J = 6.8 Hz, 6H), 1.70 (qqd, J = 7.1, 6.8, 3.3 Hz, 2H), 4.04 (ddd, J = 10.1, 7.3, 3.3 Hz, 2H), 4.61 (dd, J = 8.8, 7.3 Hz, 2H), 4.71 (dd, J = 10.1, 8.8 Hz, 62H), 7.27 (t, J = 7.7 Hz, 1H), 7.40−7.55 (m, 3H), 7.63 (d, J = 7.7 Hz, 2H), 7.83 (d, J = 7.3 Hz, 2H), 8.47 (s, 1H), 9.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.2, 19.4, 29.3, 67.3, 71.1, 121.5, 123.1, 124.7, 127.1, 128.0, 129.3, 129.5, 131.6, 153.0, 154.3, 172.4 (J_{Rh-C} = 3.4 Hz), 187.3 (J_{Rh-C} = 19.7 Hz). Anal. Found for $C_{27}H_{30}N_3O_3Cl_2Rh$: C, 52.45; H, 4.98; N, 6.82. Calcd: C, 52.44; H, 4.89; N, 6.80.

Reaction of 5b with Benzaldehyde. (Bn-Phebox)RhCl$_2$(=COCH(Ph)CH(SO$_2$-*p*-Tol)NH) (8b). (4*S*,5*S*)-8b. This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 2.57−2.67 (m, 2H), 3.32 (dd, J = 14.4, 4.1 Hz, 2H), 4.31−4.69 (m, 6H), 5.13 (d, J = 5.8 Hz, 1H), 6.89−7.94 (m, 23H), 9.77 (bs, 1H).

(4*R*,5*R*)-8b. This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 2.57−2.67 (m, 2H), 3.41 (dd, J = 13.9, 3.4 Hz, 2H), 4.31−4.69 (m, 6H), 5.04 (d, J = 4.7 Hz, 1H), 6.89−7.94 (m, 23H), 10.05 (bs, 1H).

Reaction of 5c with Benzaldehyde. (*t*-Bu-Phebox)RhCl$_2$(=COCH(Ph)CH(SO$_2$-*p*-Tol)NH) (8c). (4*S*,5*S*)-8c. This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.74 (s, 18H), 2.50 (s, 3H), 4.59−4.75 (m, 6H), 5.09 (d, J = 8.2 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 7.27−7.68 (m, 10H), 7.96 (d, J = 8.4 Hz, 2H), 9.16 (bs, 1H).

(4*R*,5*R*)-8c. This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (s, 18H), 2.49 (s, 3H), 4.65−4.88 (m, 6H), 4.99 (d, J = 7.9 Hz, 1H), 6.65 (d, J = 7.9 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.40−7.57 (m, 7H), 7.65 (d, J = 7.7 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 9.82 (bs, 1H).

(*t*-Bu-Phebox)RhCl$_2$(=COCH(Ph)CHNH) (10c). This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (s, 18H), 4.59−4.75 (m, 6H), 7.27−7.68 (m, 9H), 11.57 (bs, 1H).

Table 9. Crystallographic Data for 4b,c and 5c

	4b	4c	5c
formula	$C_{30}H_{28}N_3O_4Cl_2Rh$	$C_{24}H_{32}N_3O_4Cl_2Rh$	$C_{58}H_{72}N_6O_8Cl_4S_2Rh_2$
fw	668.38	600.35	1392.99
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
cell constants			
a, Å	14.463(2)	11.492(3)	12.963(8)
b, Å	15.594(2)	21.751(5)	21.677(8)
c, Å	13.141(2)	10.892(4)	11.052(8)
β, deg			89.98(5)
V, Å^3	2963.9(6)	2722(1)	3105(2)
Z	4	4	2
D_{calcd}, g cm^{-3}	1.498	1.464	1.490
F(000)	1360	1232	1432
μ(Mo Kα), cm^{-1}	7.94	8.55	8.26
radiation; λ, Å	Mo Kα; 0.710 69	Mo Kα; 0.710 69	Mo Kα; 0.710 69
temp, °C	23.0	23.0	23.0
$2\theta_{max}$, deg	55.1	55.0	55.0
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan width, deg	1.26 + 0.30 tan θ	1.15 + 0.30 tan θ	1.05 + 0.30 tan θ
no. of total data collected	3831	3526	7687
no. of unique data			7326 (R_{int} = 0.038)
no. of obsd rflns	2494 ($I > 3\sigma$)	2711 ($I > 3\sigma$)	4796 ($I > 3\sigma$)
no. of variables	361	307	720
residuals: R; R_w	0.042; 0.045	0.038; 0.044	0.046; 0.053

Reaction of 5a with Pivalaldehyde. (*i*-Pr-Phebox)RhCl$_2$(=COCH(*t*-Bu)CH(SO$_2$*p*-Tol)NH) (9a). (4*S*,5*S*)-9a. The product was purified by silica gel chromatography (20:1 hexane−ethyl acetate) at 0 °C in 31% yield. Mp: 174 °C dec. IR (KBr): ν 3455, 2960, 1618, 1484, 1393, 1151, 960, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80 (d, J = 6.6 Hz, 6H), 0.84 (d, J = 7.0 Hz, 6H), 1.13 (s, 9H), 2.14 (qqd, J = 7.0, 6.6, 2.9 Hz, 2H), 2.46 (s, 3H), 3.92 (dd, J = 7.9, 2.9 Hz, 2H), 4.62 (d, J = 7.9 Hz, 4H), 4.78 (d, J = 5.9 Hz, 1H), 5.46 (d, J = 5.9 Hz, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.43 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 7.7 Hz, 2H), 7.88 (d, J = 8.1 Hz, 2H), 9.32 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 19.6, 21.9, 24.9, 29.1, 34.5, 67.6, 70.7, 75.8, 95.0, 123.3, 127.6, 129.8, 130.9, 131.1, 132.0, 147.0, 173.8 (J_{Rh-C} = 3.2 Hz), 196.7 (J_{Rh-C} = 14.8 Hz), 231.6 (J_{Rh-C} = 31.8 Hz). Anal. Found for $C_{32}H_{42}N_3O_5Cl_2SRh$: C, 50.91; H, 5.59; N, 5.63. Calcd: C, 50.94; H, 5.61; N, 5.57.

(4*R*,5*R*)-9a. This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80 (d, J = 6.6 Hz, 6H), 0.85 (d, J = 7.1 Hz, 6H), 1.13 (s, 9H), 2.14 (qqd, J = 7.1, 6.6, 2.8 Hz, 2H), 2.46 (s, 3H), 3.92 (dd, J = 8.0, 2.8 Hz, 2H), 4.62 (d, J = 8.0 Hz, 4H), 4.77 (d, J = 5.8 Hz, 1H), 5.47 (d, J = 5.8 Hz, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 7.7 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 9.79 (bs, 1H).

(*i*-Pr-Phebox)RhCl$_2$(=COCH(*t*-Bu)CHNH) (11a). This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.71−0.86 (m, 12H), 1.25 (s, 9H), 1.54−1.63 (m, 2H), 3.86−3.93 (m, 4H), 4.52−4.71 (m, 2H), 6.91 (d, J = 1.7 Hz, 1H), 7.24−7.64 (m, 3H), 11.42 (bs, 1H).

Reaction of 5b with Pivalaldehyde. (Bn-Phebox)RhCl$_2$(=COCH(*t*-Bu)CH(SO$_2$*p*-Tol)NH) (9b). (4*S*,5*S*)-9b. This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11 (s, 9H), 2.28 (s, 3H), 2.45−2.63 (m, 2H), 3.13 (dd, J = 14.4, 3.6 Hz, 2H), 4.40−4.67 (m, 6H), 4.97 (d, J = 5.9 Hz, 1H), 5.29 (d, J = 5.9 Hz, 1H), 6.93−7.91 (m, 15H), 7.81 (d, J = 8.4 Hz, 2H), 9.72 (bs, 1H).

(4*R*,5*R*)-9b. This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 (s, 9H), 2.45 (s, 3H), 2.45−2.63 (m,

Table 10. Crystallographic Data for (4*S*,5*R*)-7a, (4*R*,5*S*)-7b, (4*R*,5*R*)-8a, and 12

	(4*S*,5*R*)-**7a**	(4*R*,5*S*)-**7b**	(4*R*,5*R*)-**8a**	**12**
formula	$C_{27}H_{38}N_3O_5Cl_2Rh$	$C_{35}H_{38}N_3O_5Cl_2Rh$	$C_{34}H_{38}N_3O_5Cl_2SRh$	$C_{54}H_{60}N_6O_6Cl_4Rh_2$
fw	658.43	754.51	774.56	1236.73
cryst syst	orthorhombic	orthorhombic	orthorhombic	triclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P1$
cell constants				
a, Å	12.318(3)	13.807(5)	11.967(7)	11.594(2)
b, Å	20.576(3)	20.982(5)	11.989(8)	12.882(2)
c, Å	12.123(2)	11.610(4)	24.492(8)	9.613(1)
α, deg				92.55(1)
β, deg				92.49(1)
γ, deg				75.64(1)
V, Å^3	3072.7(9)	3363(1)	3513(2)	1388.6(4)
Z	4	4	4	1
D_{calcd}, g cm^{-3}	1.423	1.490	1.464	1.479
F(000)	1360	1552	1592	632
μ(Mo Kα), cm^{-1}	7.67	7.11	7.40	8.38
radiation; λ, Å	Mo Kα; 0.710 69	Mo Kα; 0.710 69	Mo Kα; 0.710 69	Mo Kα; 0.710 69
temp, °C	23.0	23.0	23.0	23.0
$2\theta_{max}$, deg	55.1	55.1	55.0	55.0
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan width, deg	1.10 + 0.30 tan θ	1.10 + 0.30 tan θ	1.37 + 0.30 tan θ	1.15 + 0.30 tan θ
no. of total data collected	3979	4337	4531	6691
no. of unique data				6374 (R_{int} = 0.017)
no. of obsd rflns	2774 ($I > 3\sigma$)	3401 ($I > 3\sigma$)	3848 ($I > 3\sigma$)	4597 ($I > 3\sigma$)
no. of variables	343	415	415	646
residuals: *R*; R_w	0.042; 0.047	0.042; 0.047	0.031; 0.034	0.039; 0.043

2H), 3.43 (dd, J = 14.9, 4.1 Hz, 2H), 4.40−4.67 (m, 6H), 4.77 (d, J = 4.8 Hz, 1H), 5.51 (d, J = 4.8 Hz, 1H), 6.93−7.91 (m, 15H), 7.90 (d, J = 8.4 Hz, 2H), 9.84 (bs, 1H).

(Bn-Phebox)RhCl$_2$(=COCH(*t*-Bu)CHNH) (11b). This complex could not be isolated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (s, 9H), 2.45−2.63 (m, 2H), 2.96 (dd, J = 13.4, 3.0 Hz, 2H), 4.40−4.67 (m, 6H), 6.93−7.91 (m, 14H), 11.68 (bs, 1H).

Oxazoline Formation from a Carbene Complex. *trans*-4(*p*-Tolylsulfonyl)-5-phenyl-2-oxazoline (14). To a stirred solution of carbene complex (4*S*,5*S*)-**8a** or (4*R*,5*R*)-**8a** in dichloromethane was added $AgBF_4$ (2.1 equiv) at 20 °C, and the reaction mixture was stirred for 1.5 h at that temperature. Pulification by alumina (Al_2O_3) chromatography (benzene) gave *trans*-4-(*p*-tolylsulfonyl)-5-phenyl-2-oxazoline in 7% yield for (4*S*,5*S*)-**14** or 41% yield for (4*R*,5*R*)-**14**, respectively. IR (KBr): ν 3079, 2956, 1612, 1494, 1311, 1154, 1113, 948, 702, 666 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 5.04 (dd, J = 5.9, 1.6 Hz, 1H), 6.05 (d, J = 5.9 Hz, 1H), 7.22 (d, J = 1.6 Hz, 1H), 7.28−7.46 (m, 7H), 7.85 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 79.4, 92.6, 125.3, 129.1, 129.2, 129.6, 130.0, 133.2, 137.8, 145.8, 159.6. Daicel CHIRALCEL OD-H, UV detector 254 nm, hexane−*i*-PrOH (5:1), flow rate 0.5 mL/min, t_R = 19.1 min (4*S*,5*S*), 25.5 min (4*R*,5*R*). This is a known compound. The physical data are consistent with those reported.[21g]

X-ray Structure Determination and Details of Refinement. X-ray-quality crystals of **4b**,**c**, **5c**, (4*S*,5*R*)-**7a**, (4*R*,5*S*)-**7b**, (4*R*,5*R*)-**8a**, and **12** were obtained directly from the preparations described above and mounted in glass capillaries. Diffraction experiments were performed on a Rigaku AFC-7R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation; λ = 0.710 69 Å. The lattice parameters and orientation matrixes were obtained and refined from 24 machine-centered reflections with 29.52 < 2θ < 29.99° for **4b**, from 25 machine-centered reflections with 29.60 < 2θ < 29.94° for **4c**, from 25 machine-centered reflections with 29.59 < 2θ < 29.97° for **5c**, from 24 machine-centered reflections with 29.39 < 2θ < 29.98° for (4*S*,5*R*)-**7a**, from 24 machine-centered reflections with 29.60 < 2θ < 30.00° for (4*R*,5*S*)-**7b**, from 25 machine-centered reflections with 29.60 < 2θ < 29.97° for (4*R*,5*R*)-**8a**, and from 25 machine-centered reflections with 29.60 < 2θ < 29.97° for **12**. Intensity data were collected using a $\omega-2\theta$ scan technique, and 3 standard reflections were recorded every 150 reflections. The data were corrected for Lorentz and polarization effects. Relevant crystal data are given in Table 9 (for **4b**,**c** and **5c**) and Table 10 (for (4*S*,5*R*)-**7a**, (4*R*,5*S*)-**7b**, (4*R*,5*R*)-**8a**, and **12**). The structure was solved by heavy-atom Patterson methods[22] and expanded using Fourier techniques.[23] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2494 observed reflections ($I > 3\sigma(I)$) and 361 variable parameters for **4b**, on 2711 observed reflections ($I > 3\sigma(I)$) and 307 variable parameters for **4c**, on 4796 observed reflections ($I > 3\sigma(I)$) and 720 variable parameters for **5c**, on 2774 observed reflections ($I > 3\sigma(I)$) and 343 variable parameters for (4*S*,5*R*)-**7a**, on 3401 observed reflections ($I > 3\sigma(I)$) and 415 variable parameters for (4*R*,5*S*)-**7b**, on 3848 observed reflections ($I > 3\sigma(I)$) and 415 variable parameters for (4*R*,5*R*)-**8a**, and on 4597 observed reflections ($I > 3\sigma(I)$) and 646 variable parameters for **12**. Neutral atom scattering factors were taken from Cromer and Waber.[24] All calculations were performed using the teXsan[25] crystallographic software package. Final refinement details are collected in Table 9 (for **4b**,**c** and **5c**) and Table 10 (for (4*S*,5*R*)-**7a**, (4*R*,5*S*)-**7b**, (4*R*,5*R*)-**8a**, and **12**), and the numbering schemes employed are shown in Figures 2−4, which were drawn with ORTEP with 30% probability ellipsoids. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-177836 (**4b**), CCDC-177837 (**4c**), CCDC-177838 (**5c**), CCDC-177839 ((4*S*,5*R*)-**7a**), CCDC-177840 ((4*R*,5*S*)-**7b**), CCDC-177841 ((4*R*,5*R*)-**8a**), and CCDC-177842 (**12**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge

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Supporting Information Available: Tables of crystal structure parameters and details of data collection, bond angles and distances, and atomic positional and thermal parameters for **4b**,**c**, **5c**, (4*S*,5*R*)-**7a**, (4*R*,5*S*)-**7b**, (4*R*,5*R*)-**8a**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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