Synthesis and X-ray Crystal Structures of Bis(oxazolinyl)phenyl-Derived Chiral Palladium(II) and Platinum(II) and -(IV) Complexes and Their Use in the Catalytic Asymmetric Aldol-Type Condensation of Isocyanides and Aldehydes

Yukihiro Motoyama,* Hidekazu Kawakami, Kayoko Shimozono, Katsuyuki Aoki, and Hisao Nishiyama

School of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan

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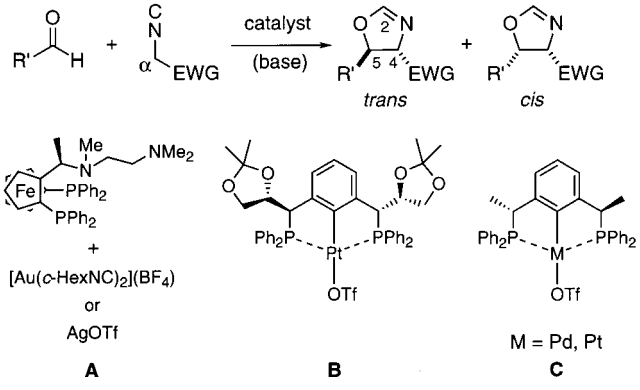
The transmetalation of (Phebox)$SnMe_3$ (**3**; Phebox = 2,6-bis(oxazolinyl)phenyl) with $PdCl_2(PhCN)_2$ or $K[PtCl_3(C_2H_4)](H_2O)$ gave (Phebox)$M^{II}Cl$ complexes (**4**, M = Pd; **5**, M = Pt) in modest to good yields. The (Phebox)$Pt^{IV}Cl_3$ complexes **8** were also synthesized by the reaction of **5** with $CuCl_2(H_2O)_2$ as an oxidant. These chloride complexes, **4**, **5**, and **8**, were in turn converted to the cationic complexes by treatment with the corresponding silver salts (AgX: X = BF_4, OTf, $OCOCF_3$). X-ray structure studies revealed that the octahedral structure of (Phebox)$Pt^{IV}Cl_2$ fragment **G** is isosteric with the (Phebox)$Rh^{III}Cl_2$ fragment **D**, and the (Phebox)M^{II} fragment **H** (M = Pd, Pt) is almost the same configuration with a square-planar structure. In these complexes, the cationic BF_4 aqua complexes (**9**, M = Pd^{II}; **10**, M = Pt^{II}; **11**, M = Pt^{IV}) were found to act as chiral catalysts for the aldol-type condensation of isocyanides and aldehydes in the presence of *i*-Pr_2NEt. Excellent *trans* diastereoselectivities and modest to good enantioselectivities were obtained in the reaction of tosylmethyl isocyanide (TosMIC, **1**) by the use of [(*i*-Pr-Phebox)$Pt^{II}(H_2O)$](BF_4) (*i*-Pr-**10**).

Introduction

The aldol-type condensation of aldehydes and isocyanides containing an electron-withdrawing group (EWG) at the α-carbon atom provides an important method for access to synthetically useful 4,5-disubstituted 2-oxazoline compounds (Scheme 1).[1] Since an asymmetric version of the condensation with a chiral Au(I) catalyst was disclosed in 1986 by Ito and Hayashi,[2] several groups have studied the catalytic systems based on the use of chiral Au^{I},[3] Ag^{I},[4] Pd^{II},[5] and Pt^{II} [5] complexes. Nevertheless, there are only three types of chiral

Scheme 1



catalysts (**A**,[2−4] **B**,[5b] **C**[5c]) with good to high enantioselectivities. These reported asymmetric catalysts have deep chiral surroundings as a common structural unit, because the enantioselective carbon−carbon bond formation is accomplished at the α-carbon atom, very distant from the metal center.

Previously, we designed an anionic "N−C−N pincer" ligand,[6] 2,6-bis(oxazolinyl)phenyl (abbreviated as Phebox), and synthesized chiral rhodium(III) aqua complexes, (Phebox)$Rh^{III}Cl_2(H_2O)$, as new types of transition-metal Lewis acids.[7,8] During the course of our studies

(1) Reviews: (a) Ugi, I. *Isonitrile Chemistry*; Academic Press: New York, 1971. (b) Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 789. (c) Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 339. Also see: (d) Schöllkopf, U.; Gerhart, F. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 805. (e) Saegusa, T.; Ito, Y.; Kinoshita, H.; Tomita, S. *J. Org. Chem.* **1971**, *36*, 3316. (f) Hoppe, D.; Schöllkopf, U. *Justus Liebigs Ann. Chem.* **1972**, *763*, 1. (g) Ito, Y.; Matsuura, T.; Saegusa, T. *Tetrahedron Lett.* **1985**, *26*, 5781. (h) Grigg, R.; Lansdell, M. I.; Thornton-Pett, M. *Tetrahedron* **1999**, *55*, 2025.

(2) (a) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405. (b) Ito, Y.; Sawamura, M.; Shirakawa, E.; Hayashizaki, K.; Hayashi, T. *Tetrahedron Lett.* **1988**, *29*, 235. (c) Sawamura, M.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* **1989**, *30*, 2247. (d) Ito, Y.; Sawamura, M.; Hamashima, H.; Emura, T.; Hayashi, T. *Tetrahedron Lett.* **1989**, *30*, 4681. (e) Hayashi, T.; Sawamura, M.; Ito, Y. *Tetrahedron* **1992**, *48*, 1999. (f) Soloshonok, V. A.; Kacharov, A. D.; Hayashi, T. *Tetrahedron* **1996**, *52*, 245.

(3) (a) Pastor, S. D.; Togni, A. *J. Am. Chem. Soc.* **1989**, *111*, 2333. (b) Togni, A.; Häusel, R. *Synlett* **1990**, 633. (c) Togni, A.; Pastor, S. D.; Rihs, G. *J. Organomet. Chem.* **1990**, *381*, C21. (d) Togni, A.; Pastor, S. D. *J. Org. Chem.* **1990**, *55*, 1649. (e) Pastor, S. D.; Togni, A. *Helv. Chim. Acta* **1991**, *74*, 905. (f) Zhou, X.-T.; Lin, Y.-R.; Dai, L.-X. *Tetrahedron: Asymmetry* **1999**, *10*, 855.

(4) Sawamura, M.; Hamashima, H.; Ito, Y. *J. Org. Chem.* **1990**, *55*, 5935.

(5) (a) Nesper, R.; Pregosin, P. S.; Püntener, K.; Wörle, M. *Helv. Chim. Acta* **1993**, *76*, 2239. (b) Gorla, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607. (c) Longmire, J. M.; Zhang, X.; Shang, M. *Organometallics* **1998**, *17*, 4374.

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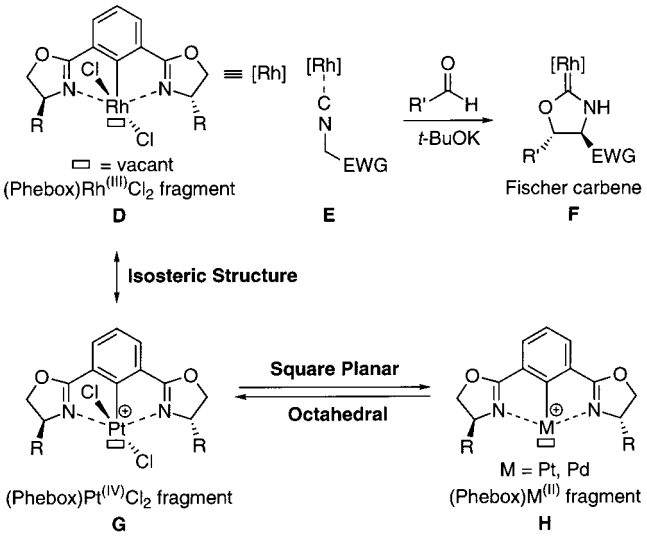
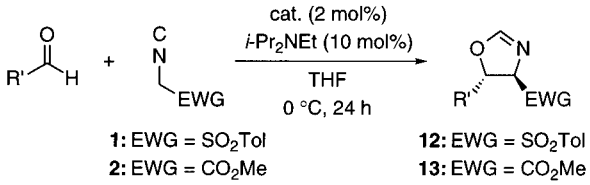
Scheme 2



on the Phebox−Rh^{III} systems, containing deep chiral pockets, we have found that isocyanide compounds can bind to the rhodium atom, forming stable isocyanide complexes (Scheme 2, **E**), and these isocyanide components on the (Phebox)$RhCl_2$ fragment **D** readily reacted with aldehydes in the presence of *t*-BuOK as a base to afford the corresponding aldol adducts as chiral Fischer carbene complexes **F** with high *trans* diastereoselectivities and modest to good diastereofacial selectivities, even in a stoichiometric manner.[9] These results clearly show that the chiral environment constructed by an octahedral structure of the (Phebox)$RhCl_2$ fragment **D** is effective for the aldol-type condensation of isocyanides and aldehydes. We also succeeded in the isolation of 2-oxazoline derivatives from these carbene complexes **F** by treatment with $AgBF_4$. This phenomenon encouraged us to use Phebox-derived cationic complexes,[10] such as Phebox−Pt^{IV} (**G**) and Phebox−Pt^{II} and −Pd^{II} complexes (**H**), for the catalytic asymmetric version of the present reaction because the (Phebox)$PtCl_2$ fragment **G** may be isosteric with the (Phebox)$RhCl_2$ fragment **D**, and the (Phebox)M^{II} fragment **H** (M = Pd, Pt) is thought to be a similar type of chiral assembly with a square-planar structure. Now we wish to report herein the synthesis and X-ray structure studies of Phebox-derived chiral Pd^{II}, Pt^{II}, and Pt^{IV} complexes[11] and asymmetric aldol-type condensations of isocyanides and aldehydes with these cationic palladium and platinum complexes (Scheme 3).

Scheme 3



Results and Discussion

1. Synthesis and X-ray Crystal Structures of Phebox−Pd^{II}, −Pt^{II}, and −Pt^{IV} Complexes. The complexes (Phebox)$Pd^{II}Cl$ (**4**) and (Phebox)$Pt^{II}Cl$ (**5**) were synthesized by transmetalation of (Phebox)$SnMe_3$ (**3**) with $PdCl_2(PhCN)_2$ or Zeise's salt, $K[PtCl_3(C_2H_4)](H_2O)$, in dichloromethane at 0 °C in 40−96% yields (Scheme 4).[12] (Phebox)$Pt^{IV}Cl_3$ complexes **8** were prepared from the corresponding Pt^{II} chloride complexes **5** by treatment of $CuCl_2(H_2O)_2$ as an oxidant in dichloroethane at 40 °C in almost quantitative yields.[13] These chloride complexes, **4**, **5**, and **8**, were in turn converted to the trifluoromethanesulfonate (OTf; **6**), trifluoroacetate ($OCOCF_3$; **7**), and tetrafluoroborate (BF_4; **9**−**11**) complexes with the corresponding silver salts in satisfactory yields (62−99%), except in the cases of the Bn-Phebox- and *t*-Bu-Phebox-derived Pt^{IV} complexes. Bn- and *t*-Bu-**11** are unstable in solution and decomposed into metallic platinum and unidentified organic products.

The complexes (*i*-Pr-Phebox)$Pd^{II}Cl$ (*i*-Pr-**4**), (*t*-Bu-Phebox)$Pt^{IV}Cl_3$ (*t*-Bu-**8**), [(*i*-Pr-Phebox)$Pd^{II}(H_2O)$](BF_4) (*i*-Pr-**9**), and (*s*-Bu-Phebox)$RhCl_2(H_2O)$ were characterized by single-crystal X-ray structure studies (Figure 1). Including the (*i*-Pr-Phebox)PtCl complex (*i*-Pr-**5**) and [(*i*-Pr-Phebox)$Pt(H_2O)$](BF_4) complex (*i*-Pr-**10**), which have been reported previously,[11] the structural features of all Pd^{II}, Pt^{II}, and Pt^{IV} complexes are almost identical. A summary of selected data is given in Table 1. The coordination geometries around the metal centers are distorted-square-planar or octahedral structures:

(6) Reviews: (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F. *Coord. Chem. Rev.* **1992**, *120*, 193. (b) Cotton, F. A.; Hong, B. *Prog. Inorg. Chem.* **1992**, *40*, 179. (c) Mayer, H. A.; Kaska, W. C. *Chem. Rev.* **1994**, *94*, 1239. (d) Rietveld, M. H. P.; Grove, D. M.; van Koten, G. *New J. Chem.* **1997**, *21*, 751. (e) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (f) Jensen, C. M. *Chem. Commun.* **1999**, 2443. (g) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

(7) (a) Motoyama, Y.; Makihara, N.; Mikami, Y.; Aoki, K.; Nishiyama, H. *Chem. Lett.* **1997**, 951. (b) Motoyama, Y.; Narusawa, H.; Nishiyama, H. *Chem. Commun.* **1999**, 131. (c) Motoyama, Y.; Koga, Y.; Nishiyama, H. *Tetrahedron* **2001**, *53*, 853. (d) Motoyama, Y.; Okano, H.; Narusawa, H.; Makihara, N.; Aoki, K.; Nishiyama, H. *Organometallics* **2001**, *20*, 1580.

(8) Phebox-coordinated palladium(II) complexes were reported; see: (a) Denmark, S. E.; Stavenger, R. A.; Faucher, A.-M.; Edwards, J. P. *J. Org. Chem.* **1997**, *62*, 3375. (b) Stark, M. A.; Richards, C. J. *Tetrahedron Lett.* **1997**, *38*, 5881. (c) Stark, M. A.; Jones, G.; Richards, C. J. *Organometallics* **2000**, *19*, 1282. Recently, a similar type of ligand, 2,6-bis(oxazolylmethyl)-4,6-dimethylbenzene (BenboxMe_2), and its coordinated rhodium(II) and rhodium(III) complexes were reported; see: (d) Gerisch, M.; Krumper, J. R.; Bergman, R. G.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 5818.

(9) Motoyama, Y.; Shimozono, K.; Aoki, K.; Nishiyama, H. *Organometallics* **2002**, *21*, 1684.

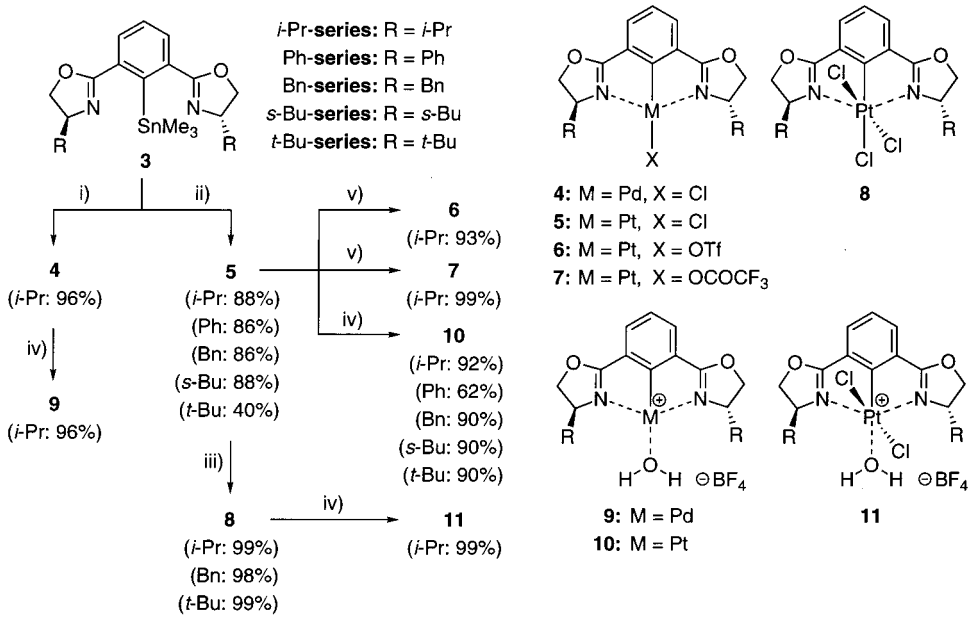
(10) van Koten reported that the cationic Pd^{II} complexes bearing N−C−N pincer ligands acted as efficient catalysts for the reaction of methyl isocyanoacetate and aldehydes; see: (a) Schlenk, C.; Kleij, A. W.; Frey, H.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 3445. (b) Kleij, A. W.; Klein Gebbink, R. J. M.; van den Nieuwenhuijzen, P. A. J.; Kooijman, H.; Lutz, M.; Spek, A. L.; van Koten, G. *Organometallics* **2001**, *20*, 634. (c) Meijer, M. D.; Ronde, N.; Vogt, D.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2001**, *20*, 3993. (d) Albrecht, M.; Kocks, B. M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **2001**, *624*, 271. (e) Rodriguez, G.; Lutz, M.; Spek, A. L.; van Koten, G. *Chem. Eur. J.* **2002**, *8*, 46.

(11) We have previously reported the synthesis of *i*-Pr-Phebox-derived Pd^{II}, Pt^{II}, and Pt^{IV} complexes (*i*-Pr-**4**, *i*-Pr-**5**, *i*-Pr-**6**, and *i*-Pr-**8**); see: Motoyama, Y.; Mikami, Y.; Kawakami, H.; Aoki, K.; Nishiyama, H. *Organometallics* **1999**, *18*, 3584. See also ref 7a.

(12) The N−C−N pincer-ligand-coordinated Pd^{II} complexes prepared by the transmetalation of stannane or silane derivatives were reported by van Koten; see: Steenwinkel, P.; Jastrzebski, J. T. B. H.; Deelman, B.-D.; Grove, D. M.; Kooijman, H.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 5486.

(13) The Pt^{IV} complexes $[PtX_3(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (X = Cl, Br) were formed in the reaction of the square-planar Pt^{II} complex $[PtX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (X = Cl, Br) with $Cu^{II}X_2$ (X = Cl, Br); see: Terheijden, J.; van Koten, G.; de Booys, J. L.; Ubbels, H. J. C.; Stam, C. H. *Organometallics* **1983**, *2*, 1882.

Scheme 4[a]



[a] Legend: (i) $PdCl_2(PhCN)_2/CH_2Cl_2/0$ °C; (ii) $K[PtCl_3(C_2H_4)](H_2O)/CH_2Cl_2/0$ °C; (iii) $CuCl_2(H_2O)_2$/dichloroethane/40 °C; (iv) $AgBF_4$/acetone−H_2O/room temperature; (v) AgX (X = OTf, $OCOCF_3$)/CH_2Cl_2/room temperature.

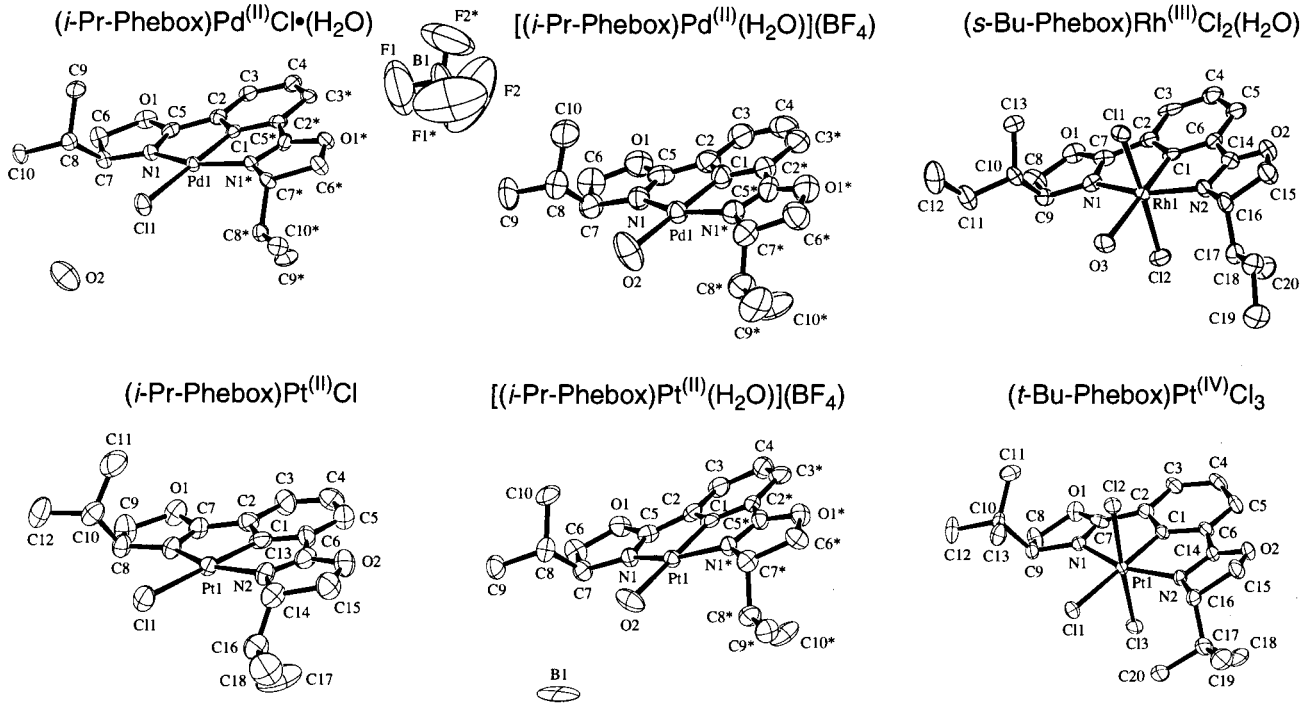


Figure 1. Molecular structures of *i*-Pr-**4**·H_2O, *i*-Pr-**5**, *t*-Bu-**8**, *i*-Pr-**9**, *i*-Pr-**10**, and (*s*-Bu-Phebox)$Rh^{III}Cl_2(H_2O)$.

N−M−N (M = Pd, Pt, Rh) angles are 158.6−159.6°. The M−N bond and the σ-bonded M−C1 distances are 2.032−2.071 and 1.90−1.96 Å, respectively. According to our expectation, these results show that the (Phebox)-$Pt^{IV}Cl_2$ fragment **G** is isosteric with the (Phebox)Rh^{III}-Cl_2 fragment **D**, and both the (Phebox)Pd^{II} and (Phebox)-Pt^{II} fragments have almost the same configuration with square-planar structures.

2. Asymmetric Aldol-Type Condensation of Isocyanides and Aldehydes. (i) Reaction of TosMIC and Benzaldehyde. The optimization of the aldol-type condensation conditions employed tosylmethyl isocyanide (TosMIC; **1**) and benzaldehyde by the use of 2 mol % of the (*S*,*S*)-Phebox-derived Pt^{IV}, Pt^{II}, and Pd^{II} complexes as chiral catalysts in the presence of 10 mol % of base at 0 °C (Table 2). First of all, the *i*-Pr-Phebox-derived cationic aqua complexes **9**−**11** gave the desired 2-oxazoline product **12a** in good to high yields, but only trace amounts of **12a** were obtained with the neutral species such as triflate (OTf) and trifluoroacetate ($OCOCF_3$) complexes (*i*-Pr-**6** and *i*-Pr-**7**) (entries 1−5). These results indicated that the OTf and $OCOCF_3$ ligands might coordinate strongly to the metal center; therefore, ligand exchange reaction from these anionic ligands to the isocyanide **1** could hardly occur. Although diastereoselectivities of the reactions with complexes

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (*i*-Pr-Phebox)PdCl·H_2O (*i*-Pr-4·H_2O), (*i*-Pr-Phebox)PtCl (*i*-Pr-5), (*t*-Bu-Phebox)$PtCl_3$ (*t*-Bu-8), (*s*-Bu-Phebox)$RhCl_2(H_2O)$, [(*i*-Pr-Phebox)Pd(H_2O)](BF_4) (*i*-Pr-9), and [(*i*-Pr-Phebox)Pt(H_2O)](BF_4) (*i*-Pr-10)

	i-Pr-**4**·H_2O	*i*-Pr-**5**[a]	*t*-Bu-**8**	(*s*-Bu-Phebox)$RhCl_2(H_2O)$[b]	*i*-Pr-**9**	*i*-Pr-**10**[a]
M−C1	1.92(1)	1.928(10)	1.96(1)	1.90(1)	1.95(1)	1.96(3)
M−N1	2.053(9)	2.032(10)	2.065(8)	2.033(9)	2.069(10)	2.04(2)
M−N2(N1*)	2.053(9)	2.035(10)	2.065(8)	2.071(1)	2.069(10)	2.04(2)
M−Cl1	2.391(3)	2.379(3)	2.417(3)	2.326(3)		
M−Cl2			2.312(3)	2.326(4)		
M−Cl3			2.314(3)			
M−O				2.273(8)	2.15(1)	2.15(2)
N1−M−N2(N1*)	159.6(5)	158.6(5)	159.3(3)	159.1(4)	158.8(5)	159(1)

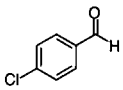
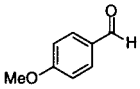
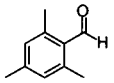
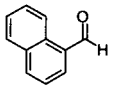
[a] Reference 11 (*i*-Pr-**5**, CCDC-179828; *i*-Pr-**10**, CCDC-179829). [b] One of the two independent crystal structures.

Table 2. Asymmetric Aldol-Type Condensation of TosMIC (1) and Benzaldehyde with Various Phebox Complexes[a]

entry	complex	amine	% yield	% *trans*[b]	% ee[c]
1	*i*-Pr-**11**	*i*-Pr_2NEt	99	>99	25
2	*i*-Pr-**10**	*i*-Pr_2NEt	99	>99	68
3	*i*-Pr-**9**	*i*-Pr_2NEt	58	>99	57
4	*i*-Pr-**6**	*i*-Pr_2NEt	6	>99	
5	*i*-Pr-**7**	*i*-Pr_2NEt	5	>99	
6[d]	*i*-Pr-**10**	*i*-Pr_2NEt	99	>99	53
7	Ph-**10**	*i*-Pr_2NEt	92	>99	<3
8	Bn-**10**	*i*-Pr_2NEt	85	>99	23
9	*s*-Bu-**10**	*i*-Pr_2NEt	87	>99	32
10	*t*-Bu-**10**	*i*-Pr_2NEt	<2		
11	*i*-Pr-**10**	*n*-Bu_3N	99	>99	57
12	*i*-Pr-**10**	Et_3N	99	>99	46
13	*i*-Pr-**10**	pyrrolidine-*N*-Me	95	>99	46
14	*i*-Pr-**10**	DABCO	99	>99	41

[a] All reactions were carried out using 0.01 mmol of Phebox complex, 0.05 mmol of amine, 0.5 mmol of TosMIC (**1**), and 0.6 mmol of benzaldehyde in 2 mL of THF at 0 °C for 24 h. [b] Determined by ^1H NMR analysis. [c] Determined by HPLC analysis using Daicel CHIRALCEL OD-H. [d] At −20 °C for 24 h.

Table 3. Asymmetric Aldol-Type Condensation of TosMIC (1) and Various Aldehydes with *i*-Pr-10[a]

entry	aldehyde	product	% yield	% *trans*[b]	% ee[c]	config.[d]
1		**12a**	99	>99	68	4*S*,5*S*
2		**12b**	99	>99	25	4*S*,5*S*
3		**12c**	99	>99	31	4*S*,5*S*
4		**12d**	99	>99	70	-
5		**12e**	91	>99	71	-
6		**12f**	99	>99	53	-
7		**12g**	60	>99	75	4*S*,5*S*

[a] All reactions were carried out using 0.01 mmol of *i*-Pr-**10**, 0.05 mmol of *i*-Pr_2NEt, 0.5 mmol of TosMIC (**1**), and 0.6 mmol of aldehyde in 2 mL of THF at 0 °C for 24 h. [b] Determined by ^1H NMR analysis. [c] Determined by HPLC analysis using Daicel CHIRALCEL OD-H or CHIRALPAK AD. [d] Assignment by comparison of the sign of optical rotation with the reported value; see the Experimental Section.

9−**11** were perfectly *trans*, enantiomeric excesses of the obtained **12a** with square-planar Pt^{II} and Pd^{II} complexes (68% ee for *i*-Pr-**10** and 57% ee for *i*-Pr-**9**) were higher than that with *i*-Pr-**11** of octahedral geometry (25% ee), which is isosteric with the (Phebox)$RhCl_2$ fragments **D**. The enantioselectivity of the reaction with *i*-Pr-**10** did not improve at −20 °C (entry 6). The substituent on the oxazoline rings had a great effect on the chemical yields and percent ee's (entry 2 vs entries 6−9). The reaction with the *t*-Bu-Phebox-derived complex (*t*-Bu-**10**) afforded only trace amounts of **12a**. The enantioselectivities using Ph-, Bn-, and *s*-Bu-**10** were remarkably decreased. We also examined the effect of amine on enantioselectivity and found that the sterically hindered Hünig base showed higher selectivity (entries 2 and 10−13).

(ii) Reaction of TosMIC and Other Aldehydes. Table 3 summarizes the results obtained for the aldol-type condensation of TosMIC (**1**) and a variety of aldehydes with 2 mol % of the complex *i*-Pr-**10** in THF in the presence of 10 mol % of *i*-Pr_2NEt at 0 °C for 24 h. All reactions resulted in good to high yields with thorough *trans* diastereoselectivities. Despite the electronic factors, the enantioselectivities of the reaction with *para*-substituted benzaldehydes were significantly decreased (entries 2 and 3). In the reaction with *ortho*-substituted benzaldehydes, enantiomeric excesses of the corresponding 2-oxazolines **12d**,**e** were almost the same degrees as that of the benzaldehyde-derived product **12a** (entries 4 and 5). Using bulky pivalaldehyde as an aliphatic aldehyde, the enantioselectivity in the reaction reached 75% ee (entry 7). In all of the cases, the absolute stereochemistry of the obtained 2-oxazolines **12** is 4*S*,5*S*.

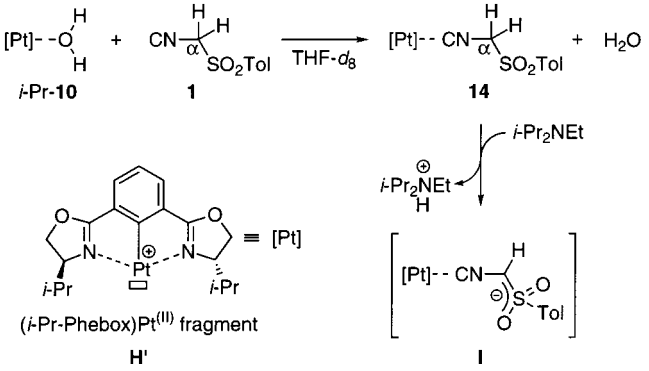
(iii) Reaction of Methyl Isocyanoacetate and Benzaldehyde. We also examined the reaction of methyl isocyanoacetate **2** and benzaldehyde catalyzed by Phebox−Pd^{II} and −Pt^{II} aqua complexes **9** and **10** (Table 4). Both of the *i*-Pr-Phebox-derived Pd^{II} and Pt^{II} complexes *i*-Pr-**9** and *i*-Pr-**10** showed remarkably low enantioselectivities (∼14% ee; entries 1 and 2). The reaction with [(Bn-Phebox)$Pt^{II}(H_2O)$](BF_4) (Bn-**10**) afforded the oxazoline **13** in almost quantitative yield with a *trans*/*cis* ratio of 87:13 (entry 3). The *trans* isomer proved to be 36% ee with an 4*R*,5*S* configuration,[2a] which is the same π-face selectivity at the carbonyl group as in the case of TosMIC (**1**). The enantiomeric excess of the product **13** was slightly increased (41% ee) when the reaction temperature was lowered to 0 °C (entry 4). In comparison to TosMIC (**1**), however, both the diastereo- and enantioselectivity are at low levels in the reaction of **2**.

Table 4. Asymmetric Aldol-Type Condensation of Methyl Isocyanoacetate (2) and Benzaldehyde with Phebox−Pd^{II} and −Pt^{II} Aqua Complexes 9 and 10[a]

entry	complex	conditions	% yield	*trans*/*cis*[b] (% ee)[c]
1	*i*-Pr-**9**	room temp, 4 h	>99	80 (<3):20
2	*i*-Pr-**10**	room temp, 5 h	99	86 (14):14
3	Bn-**10**	room temp, 5 h	99	87 (36):13
4	Bn-**10**	0 °C, 6 h	91	87 (41):13

[a] All reactions were carried out using 0.01 mmol of Phebox complex, 0.05 mmol of *i*-Pr_2NEt, 0.6 mmol of methyl isocyanoacetate (**2**), and 0.5 mmol of benzaldehyde in 2 mL of THF. [b] Determined by ^1H NMR analysis. [c] Determined by capillary GLC analysis using Astec Chiraldex G-TA (30M) and by HPLC analysis using Daicel CHIRALCEL OD-H.

Scheme 5



3. Mechanistic Studies. (i) NMR Studies of the Reaction Intermediate. To obtain information about the reaction intermediate, we first checked the complexation between [(*i*-Pr-Phebox)$Pt^{II}(H_2O)$](BF_4) (*i*-Pr-**10**) and TosMIC (**1**) (Scheme 5).[14] The ^1H NMR spectrum of the 1:1 mixture of *i*-Pr-**10** (0.017 mmol) and TosMIC (0.017 mmol) in THF-d_8 (0.7 mL) showed formation of the isocyanide complex **14** (>98%). Because of its potentially diastereotopic environments, the signals for the α-methylene protons of bound TosMIC to the chiral (Phebox)Pt^{II} fragment **H′** can be observed as two nonequivalent AB patterns.[9,14] However, the ^1H NMR spectrum for **14** shows the equivalent C$H_2$$SO_2$-Tol signal at lower field with $^{197}Pt-^1H$ coupling (δ 5.72 ppm, J_{Pt-H} = 10.3 Hz) than the uncomplexed (free) one (δ 5.01 ppm). These results suggested that the rotation along the $C_\alpha-N_{isocyanide}$ bond is faster than the NMR time scale for the TosMIC complex **14**. Addition of aldehydes to this mixture did not cause a detectable change of the ^1H NMR spectrum, indicating that aldehyde is hardly coordinated to the platinum atom. While *i*-Pr_2NEt was added to the catalyst−TosMIC solution, the signals due to the formed isocyanide complex **14** gradually faded and the resulting spectrum showed a complicated mixture. It is known that the α-isocyano carbanion species are thermolabile and easily decomposed between −60 and 0 °C.[1] Therefore, we assumed that an enolate complex such as **I** is formed immediately via deprotonation of TosMIC's α-proton bound to the (Phebox)Pt fragment **H′** by Hünig's base.

(ii) Transition State Assembly. Since the relative stereochemistry of the obtained 2-oxazolines **13** is *trans*, the chiral enolates **I** bound to the Pt^{II} atom react *trans*

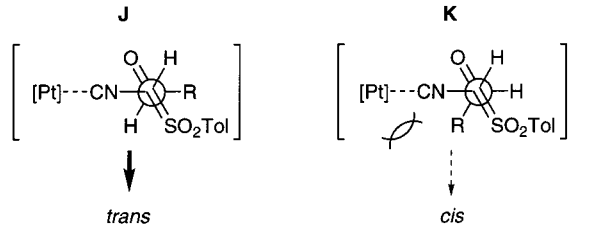


Figure 2. Antiperiplanar transition states **J** and **K**.

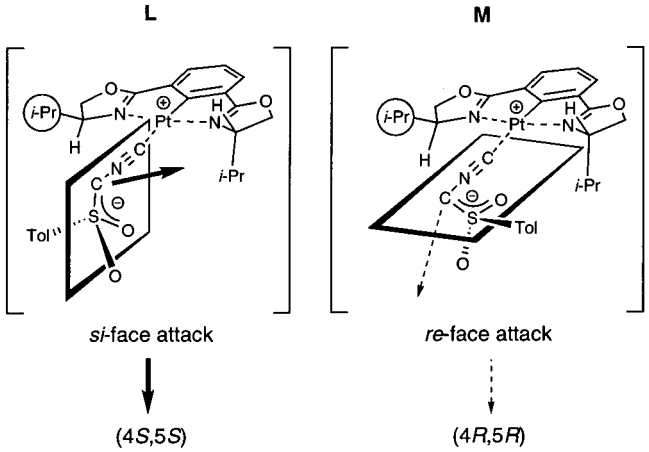


Figure 3. Structures of the enolate complexes **L** (left) and **M** (right).

selectively with aldehydes. This *trans*-selective reaction of the enolate **I** with aldehydes can be attributed to the *gauche* interaction between the R groups of aldehydes and the isocyano moiety bound to the bulky (*i*-Pr-Phebox)Pt^{II} fragment **H′** in antiperiplanar transition states (Figure 2, **J** vs **K**).

The possible structures of the TosMIC-derived Pt^{II}−enolate complexes are shown in Figure 3. The observed 4*S*,5*S* stereochemistry of the obtained 2-oxazolines **13** using (*S*,*S*)-[(*i*-Pr-Phebox)$Pt^{II}(H_2O)$](BF_4) complex (*i*-Pr-**10**) can be unambiguously explained by the intermediate **L**, whose structure is similar to that of the Phebox−Rh^{III} system with the octahedral geometry.[9] The enolate plane bound to the Pt^{II} atom is perpendicular to the Phebox plane, and the *re* face of the enolate is masked by one *i*-Pr substituent on the oxazoline rings. The aldehydes attacked the exposed *si* face of the bound enolate; therefore, the 4*S*,5*S* product was obtained. If the bound enolate plane was placed almost parallel to the Phebox plane (**M**), the opposite 4*R*,5*R* product would be obtained as the major isomer.

The reason the square-planar Pt^{II} complex shows much higher enantioselectivity than does the octahedral Pt^{IV} complex is unclear. Considering the effect of Hünig's bases on the enantioselectivities, we assumed that the location of an ammonium salt forming deprotonation from the isocyanide is playing a key role in the stereoselection by interaction with the formed enolate. A similar hypothesis is described in the ferrocenylphosphine-derived Au(I) system by Hayashi and Ito; the amino group is located close to the isocyanide bound to the metal, and therefore, the arrangement of the enolate is controlled (Scheme 1, **A**).[2e,14]

Conclusion

On the basis of our previous work using the Phebox−Rh^{III} system, we have sought to adopt the Phebox-

(14) Similar NMR studies of chiral isocyanide complexes were reported; see: Sawamura, M.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* **1990**, *31*, 272. See also refs 3d and 5a.

derived cationic palladium(II) and platinum(II) and -(IV) complexes for the catalytic asymmetric aldol-type condensation of isocyanides and aldehydes. We have described the synthesis of a series of Phebox−Pd^{II}, −Pt^{II}, and −Pt^{IV} complexes, and X-ray structure studies including the (Phebox)$Rh^{III}Cl_2(H_2O)$ complex revealed that the octahedral structure of the (Phebox)$Pt^{IV}Cl_2$ fragment is isosteric with the (Phebox)$Rh^{III}Cl_2$ fragment, and the (Phebox)M^{II} fragment (M = Pd, Pt) is almost the same configuration with a square-planar structure. We have found that the cationic aqua complexes, especially the [(*i*-Pr-Phebox)$Pt^{II}(H_2O)$](BF_4) complex with a square-planar structure, acted as efficient asymmetric catalysts for the aldol-type condensation of isocyanides and aldehydes. We also elucidated that the obtained 4*S*,5*S* stereochemistry of the 2-oxazolines can be attributed to the perpendicular conformation of both the enolate and the (*S*,*S*)-Phebox planes of the TosMIC-derived enolate intermediate.

Experimental Section

General Methods. Anhydrous dichloromethane and tetrahydrofuran were purchased from Kanto Chemical Co. (*p*-Tolylsulfonyl)methyl isocyanide (TosMIC) was purchased from Tokyo Chemical Industry Co., Ltd. Methyl isocyanoacetate, silver triflate, silver trifluoroacetate, and silver tetrafluoroborate were purchased from Aldrich Chemical Co. Dichloroethane was freshly distilled from CaH_2. ^1H and ^{13}C NMR spectra were measured on a Varian Inova-400 (400 MHz) spectrometer. ^1H NMR chemical shifts were described in parts per million downfield from tetramethylsilane as an internal standard (δ 0) in $CDCl_3$, unless otherwise noted. ^{13}C NMR chemical shifts were expressed 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 instrument. High-performance liquid chromatography (HPLC) analyses were performed with a JASCO PU-980 HPLC pump, UV-975 and 980 UV/VIS detector, and CO-966 column thermostat (at 25 °C) using Daicel CHIRALCEL OD-H and CHIRALPAK AD columns. Optical rotations were measured on a JASCO DIP-140 polarimeter. Column chromatography was performed with silica gel (Merck, Art. No. 7734) and with Al_2O_3 (Merck, Art. No. 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)$SnMe_3$ (**3**) was prepared by our method.[7d]

$PdCl(PhCN)_2$[15] and $K[PtCl_3(C_2H_4)](H_2O)$[16] were prepared by the literature methods.

(*s*-Bu-Phebox)Br. This compound was prepared from (2*S*,3*S*)-2-amino-3-methylpentan-1-ol and 2-bromo-*m*-xylene according to our method.[7d] Colorless oil. $[\alpha]_D^{20} = -76.4°$ (*c* 1.06, $CHCl_3$). IR (neat): ν 2962, 2876, 1664, 1584, 1460, 1363, 1131, 971, 730 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, J = 6.8 Hz, 6H), 0.96 (t, J = 7.4 Hz, 6H), 1.27 (m, 2H), 1.61 (m, 2H), 1.77 (m, 2H), 4.18 (dd, J = 8.0, 7.9 Hz, 2H), 4.28 (ddd, J = 9.6, 8.0, 5.8 Hz, 2H), 4.43 (dd, J = 9.6, 7.9 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.64 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 14.5, 26.1, 39.0, 70.1, 71.6, 121.4, 127.0, 132.4, 132.7, 163.0. Anal. Found for $C_{20}H_{27}N_2O_2Br$: C, 59.02; H, 6.61; N, 6.93. Calcd: C, 58.97; H, 6.68; N, 6.88.

(*s*-Bu-Phebox)$SnMe_3$ (*s*-Bu-3). This compound was prepared from (*s*-Bu-Phebox)Br and Me_3SnCl according to our method.[7d] Colorless oil. IR (neat): ν 2963, 1651, 1459, 1351, 1248, 1131, 979, 770 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.20 (s, satellite J_{Sn-H} = 55.5, 53.0 Hz, 9H), 0.87 (d, J = 6.7 Hz, 6H), 0.95 (t, J = 7.3 Hz, 6H), 1.25 (m, 2H), 1.61−1.75 (m, 4H), 4.07 (dd, J = 9.1, 7.7 Hz, 2H), 4.14 (ddd, J = 9.2, 9.1, 6.6 Hz, 2H), 4.43 (dd, J = 9.2, 7.7 Hz, 2H), 7.35 (t, J = 7.7 Hz, satellite J_{Sn-H} = 5.7 Hz, 1H), 7.89 (d, J = 7.7 Hz, satellite J_{Sn-H} = 12.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.6 (satellite J_{Sn-C} = 386.5, 368.8 Hz), 11.4, 14.9, 26.2, 39.5, 70.8, 71.9, 127.8 (satellite J_{Sn-C} = 8.2 Hz), 130.8 (satellite J_{Sn-C} = 31.5 Hz), 136.2 (satellite J_{Sn-C} = 19.1 Hz), 147.3 (satellite J_{Sn-C} = 465.1, 443.4 Hz), 165.3 (satellite J_{Sn-C} = 14.5 Hz). Anal. Found for $C_{23}H_{36}N_2O_2Sn$: C, 56.26; H, 7.37; N, 5.66. Calcd: C, 56.23; H, 7.39; N, 5.70.

(*s*-Bu-Phebox)$RhCl_2(H_2O)$. This compound was prepared from (*s*-Bu-Phebox)$SnMe_3$ (*s*-Bu-**3**) and $[RhCl(c\text{-octene})_2]_2$ according to our method.[7e] Single crystals for the X-ray diffraction study were obtained from hexane−ether at room temperature. Pale yellow solid. Mp: 134 °C dec. IR (KBr): ν 3763, 2962, 2925, 1620, 1487, 1397, 962 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (d, J = 6.8 Hz, 6H), 0.98 (t, J = 7.3 Hz, 6H), 1.22 (m, 2H), 1.31 (m, 2H), 2.41 (m, 2H), 2.89 (bs, 2H), 4.37 (ddd, J = 10.1, 6.8, 2.9 Hz, 2H), 4.67 (dd, J = 8.8, 6.8 Hz, 2H), 4.74 (dd, J = 10.1, 8.8 Hz, 2H), 7.28 (t, J = 7.7 Hz, 1H), 7.57 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0, 12.5, 27.0, 36.0, 66.1, 71.2, 123.4, 128.1, 131.5, 170.7 (J_{Rh-C} = 3.8 Hz), 179.4 (J_{Rh-C} = 22.8 Hz). Anal. Found for $C_{20}H_{29}N_2O_3Cl_2Rh$: C, 46.33; H, 5.54; N, 5.32. Calcd: C, 46.26; H, 5.63; N, 5.39.

(*i*-Pr−Phebox)PdCl (*i*-Pr-4). White solids. Mp: 244−246 °C dec. IR (KBr): ν 2954, 1614, 1483, 1398, 1149, 957 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.83 (d, J = 6.8 Hz, 6H), 0.94 (d, J = 7.2 Hz, 6H), 2.83 (dqq, J = 3.6, 7.2, 6.8 Hz, 2H), 4.36 (ddd, J = 8.0, 7.6, 3.6 Hz, 2H), 4.64 (d, J = 7.6 Hz, 2H), 4.65 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 19.0, 29.1, 67.0, 71.2, 124.0, 127.0, 129.6, 168.0, 173.9. Anal. Found for $C_{18}H_{23}N_2O_2ClPd$: C, 48.90; H, 5.18; N, 6.37. Calcd: C, 48.99; H, 5.25; N, 6.35. Single crystals for the X-ray diffraction study were obtained as (*i*-Pr−Phebox)PdCl•(H_2O) from dichloromethane−hexane at room temperature. Anal. Found for $C_{18}H_{23}N_2O_2ClPd{\cdot}H_2O$: C, 46.95; H, 5.49; N, 6.07. Calcd: C, 47.08; H, 5.49; N, 6.10.

(*i*-Pr−Phebox)PtCl (*i*-Pr-5). Yellow solids. Single crystals for the X-ray diffraction study were obtained from ethyl acetate at room temperature. Mp: 261−263 °C dec. IR (KBr): ν 2956, 1603, 1484, 1401, 1330, 1148, 959 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.79 (d, J = 6.8 Hz, 6H), 0.96 (d, J = 7.2 Hz, 6H), 2.90 (dqq, J = 7.2, 6.8, 3.6 Hz, 2H), 4.42 (dt, J = 7.8, 3.6 Hz, 2H), 4.76 (d, J = 7.8 Hz, 4H), 7.18 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 7.6 Hz, satellite J_{Pt-H} = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 18.8, 28.9, 67.0 (satellite, J_{Pt-C} = 34.0 Hz), 73.1 (satellite, J_{Pt-C} = 22.0 Hz), 126.0 (satellite, J_{Pt-C} = 38.5 Hz), 126.8, 131.0 (satellite, J_{Pt-C} = 23.2 Hz), 158.7 (satellite, J_{Pt-C} = 734.9 Hz), 176.8. Anal. Found for $C_{18}H_{23}N_2O_2ClPt$: C, 40.73; H, 4.31; N, 5.37. Calcd: C, 40.80; H, 4.37; N, 5.29.

(Ph-Phebox)PtCl (Ph-5). Yellow solids. Mp: >295 °C. IR (KBr): ν 2950, 1605, 1580, 1490, 1400, 1330, 1150, 960 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.79 (dd, J = 8.8, 5.6 Hz, 2H), 5.11 (dd, J = 10.0, 8.8 Hz, 2H), 5.39 (dd, J = 10.0, 5.6 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.24−7.34 (m, 10H), 7.43 (d, J = 7.6 Hz, satellite, J_{Pt-H} = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.6 (satellite, J_{Pt-C} = 34.9 Hz), 79.7 (satellite, J_{Pt-C} = 25.8 Hz), 122.2, 127.3, 127.6, 127.7, 128.4, 128.8, 139.7, 162.5, 179.8. Anal. Found for $C_{24}H_{19}N_2O_2ClPt$: C, 47.98; H, 3.09; N, 4.58. Calcd: C, 48.21; H, 3.20; N, 4.68.

(15) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 218.
(16) Chatt, J.; Searle, M. L. *Inorg. Synth.* **1957**, *5*, 210.

(Bn-Phebox)PtCl (Bn-5). Yellow solids. Mp: 292 °C dec. IR (KBr): ν 2921, 1654, 1561, 1491, 1405, 973, 671 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.04 (dd, J = 13.6, 8.0 Hz, 2H), 3.73 (dd, J = 13.6, 3.2 Hz, 2H), 4.68−4.85 (m, 6H), 7.13 (t, J = 7.2 Hz, 1H), 7.18−7.39 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.9, 63.4 (satellite, J_{Pt-C} = 34.5 Hz), 75.7 (satellite, J_{Pt-C} = 27.4 Hz), 122.3, 126.9, 127.4 (satellite, J_{Pt-C} = 40.2 Hz), 127.8 (satellite, J_{Pt-C} = 37.8 Hz), 128.7, 129.8, 136.3, 161.5 (satellite, J_{Pt-C} = 861.1 Hz), 179.5 (satellite, J_{Pt-C} = 192.4 Hz). Anal. Found for $C_{26}H_{23}N_2O_2ClPt$: C, 49.96; H, 3.85; N, 4.48. Calcd: C, 49.88; H, 3.70; N, 4.47.

(*s*-Bu-Phebox)PtCl (*s*-Bu-5). Yellow solids. Mp: 131 °C dec. IR (KBr): ν 2957, 1607, 1579, 1489, 1404, 1331, 1146, 958, 731 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.76 (d, J = 6.9 Hz, 6H), 0.99 (t, J = 7.4 Hz, 6H), 1.16−1.38 (m, 4H), 2.71 (m, 2H), 4.51 (ddd, J = 9.6, 6.1, 3.3 Hz, 2H), 4.71 (dd, J = 9.0, 6.1 Hz, 2H), 4.75 (dd, J = 9.6, 9.0 Hz, 2H), 7.14 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 7.6 Hz, satellite, J_{Pt-H} = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.6, 11.9, 26.3, 35.6, 65.6 (satellite, J_{Pt-C} = 34.3 Hz), 72.0 (satellite, J_{Pt-C} = 28.1 Hz), 122.2, 127.1 (satellite, J_{Pt-C} = 40.3 Hz), 128.0 (satellite, J_{Pt-C} = 39.2 Hz), 161.2 (satellite, J_{Pt-C} = 864.8 Hz), 178.9 (satellite, J_{Pt-C} = 193.8 Hz). Anal. Found for $C_{20}H_{27}N_2O_2ClPt$: C, 42.97; H, 4.88; N, 4.95. Calcd: C, 43.05; H, 4.88; N, 5.02.

(*t*-Bu-Phebox)PtCl (*t*-Bu-5). Yellow solids. Mp: 283−285 °C dec. IR (KBr): ν 2925, 1579, 1489, 1403, 1249, 965, 670 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 18H), 4.11 (dd, J = 8.4, 2.0 Hz, 2H), 4.67 (dd, J = 9.2, 8.4 Hz, 2H), 4.95 (dd, J = 9.2, 2.0 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.5, 35.5, 70.2 (satellite, J_{Pt-C} = 34.2 Hz), 74.4 (satellite, J_{Pt-C} = 26.2 Hz), 122.2, 127.4 (satellite, J_{Pt-C} = 38.7 Hz), 127.6 (satellite, J_{Pt-C} = 35.6 Hz), 159.7 (satellite, J_{Pt-C} = 852.4 Hz), 186.2 (satellite, J_{Pt-C} = 186.2 Hz). Anal. Found for $C_{20}H_{27}N_2O_2ClPt$: C, 43.06; H, 5.07; N, 5.05. Calcd: C, 43.05; H, 4.88; N, 5.02.

(*i*-Pr-Phebox)Pt(OTf) (*i*-Pr-6). Yellow solids. Mp: 223−224 °C dec. IR (KBr): ν 2975, 1610, 1550, 1490, 1390, 1280, 1250, 1040, 650 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80 (d, J = 7.1 Hz, 6H), 0.96 (d, J = 7.1 Hz, 6H), 2.52 (dsept, J = 7.1, 3.3 Hz, 2H), 4.47 (ddd, J = 9.8, 9.1, 3.3 Hz, 2H), 4.78 (dd, J = 9.1, 6.6 Hz, 2H), 4.80 (dd, J = 9.8, 6.6 Hz, 2H), 7.19 (t, J = 7.7 Hz, 1H), 7.33 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 18.5, 29.1, 66.8 (satellite, J_{Pt-C} = 31.5 Hz), 72.2 (satellite, J_{Pt-C} = 25.8 Hz), 120 0 (q, J_{C-F} = 317.1 Hz), 123.4, 127.5 (satellite, J_{Pt-C} = 46.3 Hz), 128.0 (satellite, J_{Pt-C} = 40.1 Hz), 151.7 (satellite, J_{Pt-C} = 991.0 Hz), 178.1 (satellite, J_{Pt-C} = 214.7 Hz). Anal. Found for $C_{19}H_{23}N_2O_5SF_3Pt$: C, 35.43; H, 3.77; N, 4.25. Calcd: C, 35.46; H, 3.60; N, 4.35.

(*i*-Pr-Phebox)Pt(OCOCF$_3$) (*i*-Pr-7). Yellow solids. Mp: 273 °C dec. IR (KBr): ν 2956, 1604, 1485, 1404, 1331, 1149, 737 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (d, J = 7.0 Hz, 6H), 0.93 (d, J = 7.10 Hz, 6H), 2.23 (qqd, J = 7.1, 7.0, 3.7 Hz, 2H), 4.42 (ddd, J = 9.7, 6.0, 3.7 Hz, 2H), 4.74 (dd, J = 9.2, 6.0 Hz, 2H), 4.78 (dd, J = 9.7, 9.2 Hz, 2H), 7.16 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 18.5, 29.7, 67.4 (satellite, J_{Pt-C} = 31.8 Hz), 72.4 (satellite, J_{Pt-C} = 27.3 Hz), 117.2 (q, J_{C-F} = 290.7 Hz), 122.7, 127.3 (satellite, J_{Pt-C} = 41.0 Hz), 128.2 (satellite, J_{Pt-C} = 38.3 Hz), 157.0 (satellite, J_{Pt-C} = 900.3 Hz), 162.6 (J_{C-F} = 35.7 Hz), 178.9 (satellite, J_{Pt-C} = 201.0 Hz). Anal. Found for $C_{20}H_{23}N_2O_4F_3Pt$: C, 39.63; H, 3.87; N, 4.64. Calcd: C, 39.54; H, 3.82; N, 4.61.

(*i*-Pr-Phebox)PtCl$_3$ (*i*-Pr-8). Yellow solids. Mp: 133 °C dec. IR (KBr): ν 2925, 1614, 1493, 1415, 924, 737 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (d, J = 6.7 Hz, 6H), 1.00 (d, J = 7.2 Hz, 6H), 3.03 (dqq, J = 2.9, 7.2, 6.7 Hz, 2H), 4.57 (ddd, J = 10.3, 6.6, 2.90 Hz, 2H), 4.94 (dd, J = 9.1, 6.6 Hz, 2H), 5.00 (dd, J = 10.3, 9.1 Hz, 2H), 7.48 (t, J = 7.7 Hz, 1H), 7.68 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.8, 19.3, 28.1, 66.8 (satellite, J_{Pt-C} = 20.1 Hz), 73.1 (satellite, J_{Pt-C} = 21.5 Hz), 126.0 (satellite, J_{Pt-C} = 8.5 Hz), 126.8, 131.1 (satellite, J_{Pt-C} = 21.7 Hz), 158.6 (satellite, J_{Pt-C} = 569.8 Hz), 176.7 (satellite, J_{Pt-C} = 105.2 Hz). Anal. Found for $C_{18}H_{23}N_2O_2Cl_3Pt$: C, 35.97; H, 3.92; N, 4.65. Calcd: C, 35.98; H, 3.86; N, 4.66.

(Bn-Phebox)PtCl$_3$ (Bn-8). Yellow solids. Mp: 149 °C dec. IR (KBr): ν 2923, 1610, 1415, 942, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.82 (dd, J = 13.9, 10.8 Hz, 2H), 4,36 (dd, J = 13.9, 3.0 Hz, 2H), 4.48−5.00 (m, 6H), 7.24−7.37 (m, 10H), 7.51 (t, J = 7.7 Hz, 1H), 7.72 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.9, 63.3, 77.5, 126.1, 127.0, 127.2, 129.1, 129.4, 131.3 (satellite, J_{Pt-C} = 20.0 Hz), 136.2, 159.1 (satellite, J_{Pt-C} = 559.5 Hz), 177.1 (satellite, J_{Pt-C} = 105.5 Hz). Anal. Found for $C_{26}H_{23}N_2O_2Cl_3Pt$: C, 44.76; H, 3.31; N, 3.96. Calcd: C, 44.81; H, 3.33; N, 4.02.

(*t*-Bu-Phebox)PtCl$_3$ (*t*-Bu-8). Yellow solids. Single crystals for the X-ray diffraction study were obtained from chloroform−ether−hexane at room temperature. IR (KBr): ν 2962, 1608, 1492, 1415, 1250, 967, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (s, 18H), 4.22 (dd, J = 9.4, 3.0 Hz, 2H), 4.95 (dd, J = 9.4, 9.2 Hz, 2H), 5.14 (dd, J = 9.2, 3.0 Hz, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.70 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6, 35.5, 70.9 (satellite, J_{Pt-C} = 18.8 Hz), 76.6 (satellite, J_{Pt-C} = 18.3 Hz), 126.0, 126.7, 131.2 (satellite, J_{Pt-C} = 20.4 Hz), 157.2 (satellite, J_{Pt-C} = 557.6 Hz), 178.8 (satellite, J_{Pt-C} = 101.6 Hz). Anal. Found for $C_{20}H_{27}N_2O_2Cl_3Pt$: C, 38.14; H, 4.32; N, 4.43. Calcd: C, 38.20; H, 4.33; N, 4.45.

[(*i*-Pr-Phebox)Pd(H$_2$O)](BF$_4$) (*i*-Pr-9). White solids. Single crystals for the X-ray diffraction study were obtained from benzene−acetone at room temperature. Mp: 244−246 °C dec. IR (KBr): ν 3438, 2925, 1618, 1487, 1403, 1137, 1057, 736 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ 0.97 (d, J = 6.8 Hz, 6H), 1.05 (d, J = 7.1 Hz, 6H), 2.17 (qqd, J = 7.1, 6.8, 3.8 Hz, 2H), 4.34 (ddd, J = 8.7, 6.9, 3.8 Hz, 2H), 4.84−4.89 (m, 4H), 7.36 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 18.5, 31.4, 68.0, 73.1, 126.7, 128.9, 130.9, 163.8, 175.4. Anal. Found for $C_{18}H_{25}N_2O_3B_1F_4Pd$: C, 42.01; H, 4.81; N, 5.45. Calcd: C, 42.34; H, 4.93; N, 5.49.

[(*i*-Pr-Phebox)Pt(H$_2$O)](BF$_4$) (*i*-Pr-10). Yellow solids. Single crystals for the X-ray diffraction study were obtained from benzene−acetone at room temperature. Mp: 197−199 °C dec. IR (KBr): ν 3401, 2960, 1612, 1582, 1490, 1407, 1127, 1063, 965, 738 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ 0.83 (d, J = 6.8 Hz, 6H), 0.97 (d, J = 7.2 Hz, 6H), 2.17 (qqd, J = 7.2, 6.8, 3.2 Hz, 2H), 4.30 (dt, J = 3.2, 7.6 Hz, 2H), 4.77−4.92 (m, 4H), 7.25 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ 14.3, 18.3, 31.1, 68.0 (satellite, J_{Pt-C} = 34.0 Hz), 73.7 (satellite, J_{Pt-C} = 27.0 Hz), 125.2, 128.7 (satellite, J_{Pt-C} = 42.0 Hz), 129.3, 152.8, 180.1 (satellite, J_{Pt-C} = 207.0 Hz). Anal. Found for $C_{18}H_{25}N_2O_3BF_4Pt$: C, 36.13; H, 4.26; N, 4.69. Calcd: C, 36.08; H, 4.20; N, 4.67.

[(Ph-Phebox)Pt(H$_2$O)](BF$_4$) (Ph-10). Yellow solids. Mp: 175 °C dec. IR (KBr): ν 3494, 3032, 1609, 1490, 1407, 1331, 1060, 933, 701 cm^{-1}. Anal. Found for $C_{24}H_{21}N_2O_3BF_4Pt$: C, 43.26; H, 3.27; N, 4.26. Calcd: C, 43.20; H, 3.17; N, 4.20.

[(Bn-Phebox)Pt(H$_2$O)](BF$_4$) (Bn-10). Yellow solids. Mp: 193−194 °C dec. IR (KBr): ν 3213, 2929, 1609, 1491, 1408, 1084, 951, 735 cm^{-1}. Anal. Found for $C_{26}H_{25}N_2O_3BF_4Pt$: C, 44.92; H, 3.78; N, 3.89. Calcd: C, 44.91; H, 3.62; N, 4.03.

[(*s*-Bu-Phebox)Pt(H$_2$O)](BF$_4$) (*s*-Bu-10). Yellow solids. Mp: 92 °C dec. IR (KBr): ν 3404, 2961, 1659, 1611, 1584, 1490, 1406, 1300, 1064, 738 cm^{-1}. Anal. Found for $C_{20}H_{29}N_2O_3BF_4Pt$: C, 38.45; H, 4.68; N, 4.48. Calcd: C, 38.29; H, 4.66; N, 4.47.

[(*t*-Bu-Phebox)Pt(H$_2$O)](BF$_4$) (*t*-Bu-10). Yellow solids. Mp: 197 °C dec. IR (KBr): ν 3414, 2969, 1585, 1492, 1414, 1332, 1262, 1064, 971, 742 cm^{-1}. Anal. Found for $C_{20}H_{29}N_2O_3BF_4Pt$: C, 38.29; H, 4.69; N, 4.51. Calcd: C, 38.29; H, 4.66; N, 4.47.

[(*i*-Pr-Phebox)PtCl$_2$(H$_2$O)](BF$_4$) (*i*-Pr-11). Yellow solids. Mp: 106−108 °C dec. IR (KBr): ν 3486, 2965, 1615, 1496, 1419, 1258, 1082, 923, 740 cm^{-1}. Anal. Found for $C_{18}H_{25}N_2O_3$-

$BCl_2F_4Pt{\cdot}H_2O$: C, 31.55; H, 4.08; N, 3.82. Calcd: C, 31.41; H, 3.95; N, 4.07.

General Procedure for the Asymmetric Aldol-Type Condensation of Aldehydes and TosMIC Catalyzed with [(Phebox)Pt^{II}(H_2O)](BF_4) Complexes. To a solution of the [(Phebox)Pt^{II}(H_2O)](BF_4) complex **10** (0.01 mmol), aldehyde (0.6 mmol), and TosMIC (**1**; 97.6 mg, 0.5 mmol) in THF (2 mL) was added *N*,*N*-diisopropylethylamine (8.7 μL, 0.05 mmol) at 0 °C. After it was stirred for 24 h at that temperature, the reaction mixture was filtered through a pad of Celite and Florisil, and then the filtrate was concentrated under reduced pressure. Purification by silica gel chromatography (benzene in 1% of triethylamine) gave the 2-oxazoline: the *trans*/*cis* ratio was determined by ^{1}H NMR analysis, and the enantioselectivity was determined by chiral HPLC analysis.

4-(*p*-Tolylsulfonyl)-5-phenyl-2-oxazoline (12a). Data are as follows for the *trans* isomer. White solid. Mp: 122 °C. $[\alpha]_D^{27} = -137.8°$ (*c* 0.75, THF) for 68% ee; lit.[4] $[\alpha]_D^{20} = +212°$ (*c* 1.0−1.1, THF) for 86% ee (4*R*,5*R*). IR (KBr): ν 3079, 2956, 1612, 1494, 1311, 1154, 1113, 948, 702 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, 5:1 hexane−*i*-PrOH, flow rate 0.5 mL/min: t_R = 19.1 min (4*R*,5*R*), 25.5 min (4*S*,5*S*). Data are as follows for the cis complex. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 5.37 (dd, J = 10.2, 1.9 Hz, 1H), 5.89 (d, J = 10.2 Hz, 1H), 7.28−7.46 (m, 8H), 7.61 (d, J = 8.2 Hz, 2H).

4-*p*-Toluenesulfonyl-5-(*p*-chlorophenyl)-2-oxazoline (12b). Data are as follows for the *trans* isomer. White solid. Mp: 42 °C. $[\alpha]_D^{21} = -86.3°$ (*c* 1.00, THF) for 25% ee, lit.[4] $[\alpha]_D^{20} = +200°$ (*c* 1.0−1.1, THF) for 89% ee (4*R*,5*R*). IR (KBr): ν 1681, 1622, 1564, 1495, 1401, 1315, 1145, 1089, 819, 650 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 4.98 (dd, J = 6.0, 2.0 Hz, 1H), 6.02 (d, J = 6.0 Hz, 1H), 7.21 (d, J = 2.0 Hz, 1H), 7.27 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 78.7, 92.6, 126.6, 129.4, 129.6, 130.0, 133.0, 135.0, 136.3, 145.9, 159.3. Daicel CHIRALCEL OD-H, UV detector 254 nm, 5:1 hexane−*i*-PrOH, flow rate 0.5 mL/min: t_R = 19.5 min (4*R*,5*R*), 26.0 min (4*S*,5*S*).

4-(*p*-Tolylsulfonyl)-5-(*p*-methoxyphenyl)-2-oxazoline (12c). Data are as follows for the *trans* isomer. White solid. Mp: 128 °C. $[\alpha]_D^{22} = -163.7°$ (*c* 1.04, THF) for 31% ee; lit.[4] $[\alpha]_D^{20} = +239°$ (*c* 1.0−1.1, THF) for 79% ee (4*R*,5*R*). IR (KBr): ν 2939, 1617, 1514, 1300, 1259, 1146, 1101, 823, 708, 661 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.71 (s, 3H), 4.93 (dd, J = 6.0, 1.6 Hz, 1H), 5.89 (d, J = 6.0 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 1.6 Hz, 1H), 7.14 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 55.4, 79.5, 92.4, 114.6, 127.0, 129.6, 129.8, 129.9, 133.2, 145.7, 159.6, 160.3. Daicel CHIRALCEL OD-H, UV detector 254 nm, 5:1 hexane−*i*-PrOH, flow rate 0.5 mL/min: t_R = 16.7 min (4*R*,5*R*), 24.7 min (4*S*,5*S*).

4-(*p*-Tolylsulfonyl)-5-(*o*-methoxyphenyl)-2-oxazoline (12d). Data are as follows for the *trans* isomer. White solid. Mp: 32−38 °C. $[\alpha]_D^{22} = -166.3°$ (*c* 0.95, THF) for 70% ee. IR (KBr): ν 3074, 2945, 1614, 1494, 1148, 1117, 814, 758 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 3.80 (s, 3H), 5.17 (dd, J = 6.2, 1.6 Hz, 1H), 6.11 (d, J = 6.2 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.97 (td, J = 7.5, 1.1 Hz, 1H), 7.11 (d, J = 1.6 Hz, 1H), 7.24 (dd, J = 7.5, 1.7 Hz, 1H), 7.35−7.39 (m, 3H), 7.85 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 55.5, 77.9, 90.9, 111.2, 120.9, 124.7, 129.2, 129.7, 129.9, 131.2, 133.6, 145.5, 157.5, 159.3. Anal. Found for $C_{17}H_{17}NO_4S$: C, 61.70; H, 5.26; N, 4.16. Calcd: C, 61.61; H, 5.17; N, 4.23. Daicel CHIRALPAK AD, UV detector 254 nm, 5:1 hexane−*i*-PrOH, flow rate 1.0 mL/min: t_R = 22.9 min (major), 29.7 min (minor).

4-*p*-Toluenesulfonyl-5-mesityl-2-oxazoline (12e). *trans* isomer: white solid. Mp: 98 °C. $[\alpha]_D$22−112.6° (c 1.00, THF) for 71% ee. IR (KBr): ν 2965, 2874, 1616, 1315, 1150, 659 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3H), 2.33 (s, 6H), 2.46 (s, 3H), 5.06 (dd, J = 8.2, 1.6 Hz, 1H), 6.42 (d, J = 8.2 Hz, 1H), 6.89 (s, 1H), 7.10 (d, J = 1.6 Hz, 1H), 7.38 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1, 21.0, 21.8, 76.9, 91.0, 129.6, 129.7, 129.9, 130.6, 133.6, 137.8, 139.3, 145.7, 159.3. Anal. Found for $C_{19}H_{21}NO_3S$: C, 66.40; H, 6.16; N, 3.99. Calcd: C, 66.45; H, 6.16; N, 4.08%. Daicel CHIRALPAK AD, UV detector 254 nm, 5:1 hexane−*i*-PrOH, flow rate 1.0 mL/min. t_R = 8.5 min (major), 11.7 min (minor).

4-(*p*-Tolylsulfonyl)-5-(α-naphthyl)-2-oxazoline (12f). Data are as follows for the *trans* isomer. White solid. Mp: 107 °C. $[\alpha]_D^{19} = -19.2°$ (*c* 0.91, THF) for 53% ee. IR (KBr): ν 3047, 2977, 1616, 1511, 1305, 1113, 794, 663 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 5.20 (dd, J = 5.1, 1.5 Hz, 1H), 6.80 (d, J = 5.1 Hz, 1H), 7.34−7.42 (m, 4H), 7.46 (dd, J = 8.1, 7.3 Hz, 1H), 7.58 (dd, J = 8.2, 7.0 Hz, 1H), 7.65 (dd, J = 8.4, 7.0 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 77.8, 91.4, 122.9, 123.9, 125.2, 126.4, 127.3, 129.2, 129.6 (2C), 129.9, 130.1, 132.1, 133.4, 134.0, 145.7, 160.1. Anal. Found for $C_{20}H_{17}NO_3S$: C, 68.17; H, 5.06; N, 3.95. Calcd: C, 68.36; H, 4.88; N, 3.99. Daicel CHIRALPAK AD, UV detector 254 nm, 5:1 hexane−*i*-PrOH, flow rate 1.0 mL/min: t_R = 15.8 min (major), 24.8 min (minor).

4-(*p*-Tolylsulfonyl)-5-(*tert*-butyl)-2-oxazoline (12g). Data are as follows for the *trans* isomer. White solid. Mp: 120 °C. $[\alpha]_D^{22} = -251.1°$ (*c* 0.8, THF) for 75% ee; lit.[4] $[\alpha]_D^{20} = +321°$ (*c* 1.0−1.1, THF) for 86% ee (4*R*,5*R*). IR (KBr): ν 2964, 1672, 1615, 1472, 1308, 1153, 1129, 960, 707 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (s, 9H), 2.46 (s, 3H), 4.76 (dd, J = 5.5, 0.4 Hz, 1H), 4.83 (dd, J = 5.5, 1.5 Hz, 1H), 7.03 (dd, J = 1.5, 0.4 Hz, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 24.5, 34.1, 86.3, 86.5, 129.6, 129.9, 133.4, 145.5, 159.9. Daicel CHIRALCEL OD-H, UV detector 254 nm, 5:1 hexane−*i*-PrOH, flow rate 1.0 mL/min: t_R = 17.3 min (4*R*,5*R*), 19.6 min (4*S*,5*S*).

4-(Carbomethoxy)-5-phenyl-2-oxazoline (13). IR (KBr): ν 2954, 1742, 1626, 1438, 1205, 1106, 951, 756, 700 cm^{-1}. Data are as follows for the *trans* isomer. $[\alpha]_D^{22} = -73.3°$ (*c* 1.2, THF) for 36% ee; lit.[2a] $[\alpha]_D^{20} = +297°$ (*c* 1.2, THF) for 96% ee (4*S*,5*R*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 4.63 (dd, J = 7.9, 2.4 Hz, 1H), 5.69 (d, J = 7.9 Hz, 1H), 7.10 (d, J = 2.4 Hz, 1H), 7.30−7.44 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 53.0, 75.5, 82.3, 125.7, 128.9, 129.1, 139.0, 156.4, 171.0. Daicel CHIRALPAK AD, UV detector 254 nm, 9:1 hexane−*i*-PrOH, flow rate 1.0 mL/min: t_R = 11.7 min (4*R*,5*S*), 16.1 min (4*S*,5*R*). Astec Chiraldex G-TA (30 M), column temperature 145 °C, detection FID: t_R = 30.2 min (4*S*,5*R*), 31.5 min (4*R*,5*S*). Data are as follows for the *cis* isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.20 (s, 3H), 5.09 (dd, J = 11.2, 2.0 Hz, 1H), 5.74 (d, J = 11.2 Hz, 1H), 7.18−7.42 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.8, 72.6, 82.0, 126.3, 128.4, 128.9, 135.2, 157.6, 169.0. Daicel CHIRALPAK AD, UV detector 254 nm, 9:1 hexane−*i*-PrOH, flow rate 1.0 mL/min: t_R = 14.8 min (major), 19.4 min (minor).

X-ray Structure Determination and Details of Refinement. X-ray-quality crystals of *i*-Pr-**4**, *t*-Bu-**8**, *i*-Pr-**9**, and (*s*-Bu-Phebox)Rh^{III}Cl_2(H_2O) 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 25 machine-centered reflections with 29.20 < 2θ < 29.94° for *i*-Pr-**4**, from 25 machine-centered reflections with 29.73 < 2θ < 29.99° for *t*-Bu-**8**, from 24 machine-centered reflections with 29.24 < 2θ < 29.93° for *i*-Pr-**9**, and from 25 machine-centered

Table 5. Crystallographic Data for *i*-Pr-4·H_2O, *t*-Bu-8, *i*-Pr-9, and (*s*-Bu-Phebox)$Rh^{III}Cl_2(H_2O)$.

	i-Pr-**4**·H_2O	*t*-Bu-**8**	*i*-Pr-**9**	(*s*-Bu-Phebox)$RhCl_2(H_2O)$
formula	$C_9H_{12.50}NO_{1.50}Cl_{0.50}Pd_{0.50}$	$C_{20}H_{27}N_2O_2Cl_3Pt$	$C_{18}H_{25}N_2O_3BF_4Pd$	$C_{40}H_{58}N_4O_6Cl_4Rh_2$
fw	229.63	628.89	510.61	1038.54
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	$P2_12_12$	$P2_1$	$P2_12_12$	$P2_1$
cell constants				
a, Å	14.536(2)	7.538(2)	14.711(2)	12.440(4)
b, Å	5.947(2)	15.881(1)	6.093(2)	14.824(4)
c, Å	10.954(3)	9.6968(9)	11.719(2)	12.761(3)
β, deg	96.26(1)	103.01(2)		
V, Å^3	947.0(6)	1154.0(3)	1050.4(6)	2292.9(9)
Z	4	2	2	2
D_{calcd}, g cm^{-3}	1.611	1.810	1.614	1.504
F(000)	468	612	516	1064
μ(Mo Kα), cm^{-1}	11.40	64.20	9.40	9.98
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	55.0	55.1	55.0	55.1
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan width, deg	1.31 + 0.30 tan θ	1.10 + 0.30 tan θ	1.31 + 0.30 tanθ	0.94 + 0.30 tan θ
total no. of data collected	1447	2951	1428	5735
no. of unique data	1298 (R_{int} = 0.731)	2754 (R_{int} = 0.017)		5493 (R_{int} = 0.028)
no. of obsd rflns	854 ($I > 3\sigma$)	2555 ($I > 3\sigma$)	1257 ($I > 3\sigma$)	3727 ($I > 3\sigma$)
no. of variables	116	252	134	504
residuals: *R*; R_w	0.040; 0.047	0.026; 0.033	0.052; 0.069	0.043; 0.048

reflections with 29.56 < 2θ < 29.99° for (*s*-Bu-Phebox)$Rh^{III}Cl_2(H_2O)$. Intensity data were collected using a $\omega-2\theta$ scan technique, and three standard reflections were recorded every 150 reflections. The data were corrected for Lorentz and polarization effects. Relevant crystal data are given in Table 5. The structure was solved by heavy-atom Patterson methods[17] and expanded using Fourier techniques.[18] 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 854 observed reflections ($I > 3\sigma(I)$) and 116 variable parameters for *i*-Pr-**4**, on 2555 observed reflections ($I > 3\sigma(I)$) and 252 variable parameters for *t*-Bu-**8**, on 1257 observed reflections ($I > 3\sigma(I)$) and 134 variable parameters for *i*-Pr-**9**, and on 3727 observed reflections ($I > 3\sigma(I)$) and 504 variable parameters for (*s*-Bu-Phebox)$Rh^{III}Cl_2(H_2O)$. Neutral atom scattering factors were taken from Cromer and Waber.[19] All calculations were performed using the teXsan[20] crystallographic software package. Final refinement details are collected in Table 5 and the numbering schemes employed are shown in Figure 1, which were drawn with ORTEP using 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-121108 (*i*-Pr-**4**), CCDC-178928 (*i*-Pr-**5**), CCDC-180035 (*t*-Bu-**8**), CCDC-180036 (*i*-Pr-**9**), CCDC-178929 (*i*-Pr-**10**), and CCDC-180663 ((*s*-Bu-Phebox)$RhCl_2(H_2O)$). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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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 *i*-Pr-**4**, *t*-Bu-**8**, *i*-Pr-**9**, and (*s*-Bu-Phebox)$Rh^{III}Cl_2(H_2O)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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