Stereochemistry in Asymmetric Alkylation of Aldimine via Chiral Bis(oxazolyl)phenylplatinum Complexes

Yukihiro Motoyama, Yoshiharu Mikami, Hidekazu Kawakami, Katsuyuki Aoki, and Hisao Nishiyama*

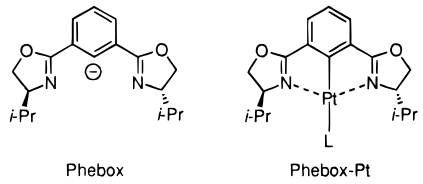
School of Materials Science, Toyohashi University of Technology Tempaku-cho, Toyohashi, Aichi 441-8580, Japan

Received April 9, 1999

Chiral (*S,S*)-(Phebox)PtCl complex **2** [Phebox = bis(oxazolyl)phenyl] and its cationic complexes (Phebox)Pt(OTf) (**3**) and [(Phebox)Pt(H_2O)](BF_4) (**4**) were synthesized by the transmetalation reaction of (Phebox)$SnMe_3$ (**1**) with K[$PtCl_3(C_2H_4)$](H_2O) and subsequent treatment with silver salts. Both cationic complexes **3** and **4** readily reacted with *N*-phenylbenzaldimine (**7**) to afford the corresponding chiral aldimine complexes [(Phebox)Pt-(aldimine)](X) (**8**, X = OTf; **9**, X = BF_4), which were subjected to alkylation with organolithium reagents resulting in 82% ee of the product amine (*S*)-**10b**.

The chemistry of chiral Lewis acids has been developed with significant successes in their organic synthesis, particularly in terms of carbon−carbon bond forming reactions.[1] Recently, many transition-metal complexes have been applied as attractive chiral Lewis acid catalysts[2] for asymmetric reactions such as the aldol reaction,[3] Diels−Alder reaction,[4] alkylation reaction,[5] and so on.[6] However, identification of their active intermediates being Lewis acid−base complexes has not yet been clarified.[7] It can be, therefore, important to simulate such intermediary species and their reactions in a given chiral stereochemical environment. We have intended to clarify the steric course during asymmetric induction by the coordination chemistry of target substrates. We now disclose new chiral platinum(II) complexes bearing a 2,6-bis(oxazolyl)phenyl (Phebox) ligand (Chart 1),[8] as a typical demonstration, which were applied to the coordination and successive alkylation of *N*-phenylbenzaldimine in order to study asymmetric induction in a stoichiometric manner.

Chart 1



The (Phebox)PtCl complex **2** was synthesized by the transmetalation reaction[9] of (Phebox)$SnMe_3$ (**1**)[8a] with the Zeise salt, K[$PtCl_3(C_2H_4)$](H_2O),[10] in dichloromethane

(1) Reviews: (a) Morrison, J. D. *Asymmetric Synthesis*; Academic Press: New York, 1984; Vol. 3B. (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994. (c) Noyori, R.; Kitamura, M. In *Modern Synthetic Methods 1989*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1989; Vol. 5. (d) Bosnich, B. *Asymmetric Catalysis*; Martinus Nijhoff Publishers: Dordrecht, The Netherlands, 1986. (e) Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1982; Vol. 8.

(2) Review: Nishiyama, H.; Motoyama, Y. In *Lewis Acid Reagents: A Practical Approach*; Yamamoto, H., Ed.; Oxford University Press: Oxford, U.K., 1999; Chapter 13.

(3) Recent representative papers: (a) Gorla, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607. (b) Evans, D. A.; Murry, J. A.; Kozlowski, M. C. *J. Am. Chem. Soc.* **1996**, *118*, 5814. (c) Evans, D. A.; MacMillan, D. W. C.; Campos, K. R. *J. Am. Chem. Soc.* **1997**, *119*, 10859. (d) Yanagisawa, A.; Matsumoto, Y.; Nakashima, H.; Asakawa, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1997**, *119*, 9319. (e) Ferraris, D.; Young, B.; Duddig, T.; Lectka, T. *J. Am. Chem. Soc.* **1998**, *120*, 4548. (f) Longmire, J. M.; Zhang, X.; Shang, M. *Organometallics* **1998**, *17*, 4374.

(4) Recent representative papers: (a) Corey, E. J.; Imai, N.; Zhang, H.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 728. (b) Kündig, E. P.; Bourdin, B.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1856. (c) Evans, D. A.; Murry, J. A.; von Matt, P.; Norcross, R. D.; Miller, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 798. (d) Yamashita, Y.; Katsuki, T. *Synlett* **1995**, 829. (e) Davies, D. L.; Fawcett, J.; Garratt, S. A.; Russel, D. R. *Chem. Commun.* **1997**, 1351. (f) Davenport, A. J.; Davies, D. L.; Fawcett, J.; Garratt, S. A.; Lad, L.; Russell, D. R. *Chem. Commun.* **1997**, 2327. (g) Kanemasa, S.; Oderaotoshi, Y.; Sakaguchi, S.; Yamamoto, H.; Tanaka, J.; Wada, E. Curran, D. P. *J. Am. Chem. Soc.* **1998**, *120*, 3074. (h) Schaus, S. E.; Branalt, J.; Jacobsen, E. N. *J. Org. Chem.* **1998**, *63*, 403. (i) Bruin, M. E.; Kündig, E. P. *Chem. Commun.* **1998**, 2635. (j) Kündig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1220.

(5) Kulawiec, R. J.; Crabtree, R. H. *Organometallics* **1988**, *7*, 1891.

(6) (a) Yanagisawa, A.; Nakashima, H.; Ishiba, A.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, *118*, 4723. (b) Stark, M. A.; Richards, C. J. *Tetrahedron Lett.* **1997**, *38*, 5881. (c) Drury, W. J., III, Ferraris, D.; Cox, C.; Young, B. Lectka, T. *J. Am. Chem. Soc.* **1998**, *120*, 11006. (d) Kanemasa, S.; Oderaotoshi, Y.; Tanaka, J.; Wada, E. *J. Am. Chem. Soc.* **1998**, *120*, 12355.

(7) For analysis of chiral Lewis acid−base complexes, see NOE analysis: (a) Corey, E. J.; Sarsher, S. *J. Am. Chem. Soc.* **1992**, *114*, 7938. (b) Corey, E. J.; Loh, T.-P.; Roper, T. D.; Azimioara, M. D.; Noe, M. C. *J. Am. Chem. Soc.* **1992**, *114*, 8290. (c) Ishihara, K.; Gao, Q.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 10412. See also X-ray analysis: (d) Knight, D. A.; Dewey, M. A.; Stark, G. A.; Bennet, B. K.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4523. (e) Gothelf, K. V.; Hazell, R. D.; Jørgensen, K. A. *J. Am. Chem. Soc.* **1995**, *117*, 4435. (f) Evans, D. A.; Kozlowski, M. C.; Murry, J. A.; Burgey, C. S.; Campos, K. R.; Connell, B. T.; Staples, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 669. Reference 4j.

(8) (a) Motoyama, Y.; Makihara, N.; Mikami, Y.; Aoki, K.; Nishiyama, H. *Chem. Lett.* **1997**, 951. Recently, the Phebox−Pd complexes were reported; see: (b) Denmark, S. E.; Stavenger, R. A.; Faucher, A.-M.; Edwards, J. P. *J. Org. Chem.* **1997**, *62*, 3375. Reference 6b.

(9) Recently, the N−C−N type ligand-coordinated Pd 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.

(10) Using $PtCl_2(PhCN)_2$, this transmetalation reaction could not proceed and (Phebox)$SnMe_3$ (**1**) was recovered quantitatively. Similar transmetalation with stannane derivatives and $PtCl_2$(COD) was examined by van Koten *et al.*, but the corresponding Pt complex could not be obtained; see ref 9.

10.1021/om990251k CCC: $18.00
Publication on Web 08/06/1999

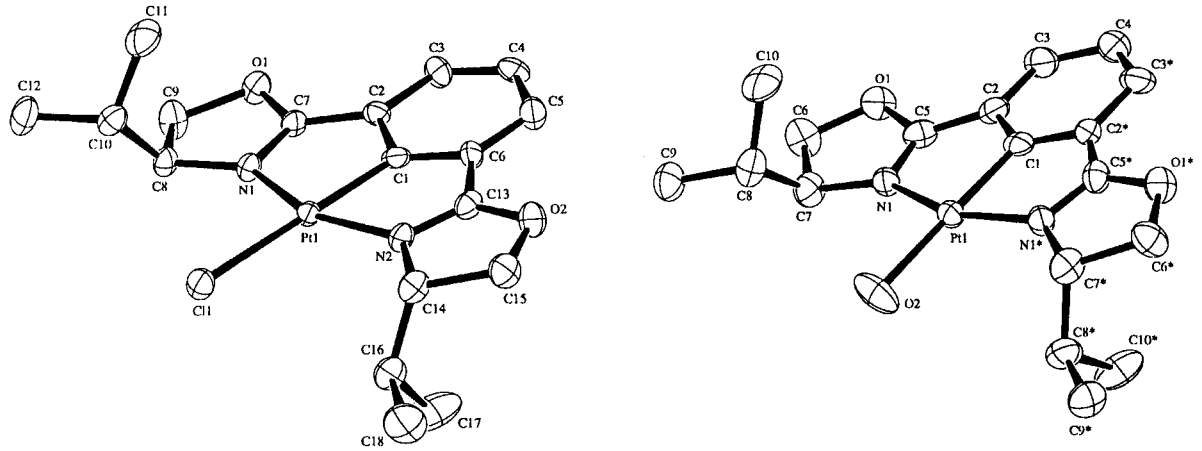
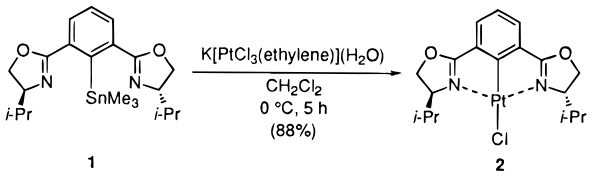
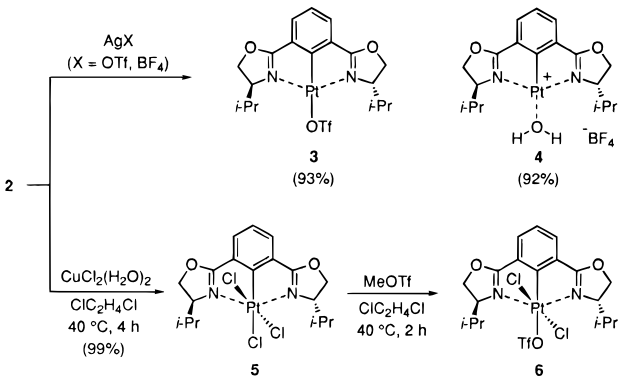


Figure 1. Molecular structures of (Phebox)PtCl complex **2** and [(Phebox)Pt(H_2O)](BF_4) complex **4**.

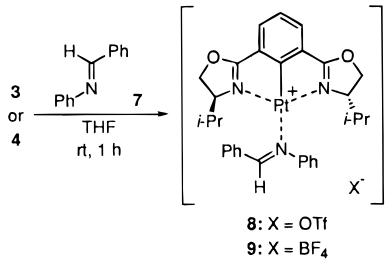
Scheme 1



Scheme 2



Scheme 3



at 0 °C. Its purification was performed by silica gel chromatography at 0 °C to give **2** as an air-stable pale yellow solid in 88% yield (Scheme 1). The chloride complex **2** was in turn converted to the corresponding trifluoromethanesulfonate (OTf, **3**) and tetrafluoroborate (BF_4, **4**) complexes with silver salts in satisfactory yields. The (Phebox)$PtCl_3$ complex **5** was synthesized from the Pt(II) complex **2** by the treatment of $CuCl_2(H_2O)_2$ in dichloroethane at 40 °C for 4 h;[11] then the reaction of **5** with MeOTf (methyl trifluoromethanesulfonate)[12] gave the (Phebox)$PtCl_2$(OTf) complex **6**[13] (Scheme 2).

The (Phebox)PtCl complex **2** and [(Phebox)Pt(H_2O)](BF_4) complex **4** were also characterized by single-crystal X-ray structure studies (Figure 1).[14] The platinum coordination geometry is almost planar, but the N−Pt−N angles are slightly distorted (158.6° at **2** and 159° at **4**). The σ-bonded Pt−C_{ipso} bond distances are 1.928 and 1.96 Å. The bond lengths between Pt and the oxazoline's nitrogens are 2.032 and 2.035 Å at **2** and 2.04 Å at **4**.

We have already reported that the Phebox−Rh(III) complexes catalyzed the allylation reaction of aldehydes with allyltin reagents as a chiral transition-metal Lewis acid,[15] so we expected these complexes **3**, **4**, and **6** to act in a similar fashion. However, the allylation reaction did not proceed, and furthermore, these complexes could not capture benzaldehyde based on the ^{1}H NMR studies. Therefore, we adopted *N*-phenylbenzaldimine (**7**) to provide the spontaneous production of the corresponding aldimine complexes **8** and **9** (Scheme 3). On the basis of the ^{1}H NMR spectra of these aldimine complexes, no dissociation of the bound aldimine was observed in $CDCl_3$ at ambient temperature (*H*−C═N; δ = 8.46 ppm for free **7**; 9.53 ppm, satellite J_{Pt-H} = 51.3 Hz for **8** and **9**). The C_2-symmetric chiral environment of Phebox can contribute to form only one isomer of these aldimine complexes. The solution of the aldimine complexes were then filtered through a pad of Celite and Florisil to remove the Phebox−Pt complexes to give free aldimine without isomerization to *cis*-**7**. Therefore, both phenyl substituents on each C═N terminus of the bound

(11) The Pt(IV) complexes [$PtX_3(C_6H_3(CH_2NMe_2)_2$-*o*,*o*′] (X = Cl, Br) were formed in the reaction of the square planar Pt(II) complex [PtX-($C_6H_3(CH_2NMe_2)_2$-*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.

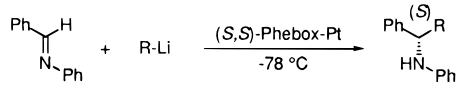
(12) The reaction of MeOTf with $SbCl_5$ leads to formation of MeCl; see: Binder, G. E.; Schmidt, A. *Z. Anorg. Allg. Chem.* **1980**, *467*, 197.

(13) The ^{1}H NMR spectrum showed the C_2-symmetric structure, and the IR spectrum showed the peaks derived from the S═O bond, so we assigned the location of the OTf ligand at the equatorial position; see Experimental Section.

(14) The selected bond distances (Å) and angles (deg). Complex **2**: Pt(1)−Cl(1), 2.379(3); Pt(1)−N(1), 2.032(10); Pt(1)−N(2), 2.035(10); Pt(1)−C(1), 1.928(10); N(1)−C(7), 1.30(1); N(2)−C(13), 1.28(2); Cl(1)−Pt(1)−N(1), 99.3(3); Cl(1)−Pt(1)−N(2), 102.0(3); N(1)−Pt(1)−C(1), 80(1); N(2)−Pt(1)−C(1), 78(1); Cl(1)−Pt(1)−C(1), 179(1); N(1)−Pt(1)−N(2), 158.6(4). Complex **4**: Pt(1)−O(2), 2.15(2); Pt(1)−N(1), 2.04(2); Pt(1)−C(1), 1.96(3); N(1)−C(5), 1.30(3); O(2)−Pt(1)−N(1), 100.3(6); C(1)−Pt(1)−N(1), 79.7(6); O(2)−Pt(1)−C(1), 180.0000(2); N(1)−Pt(1)−N(1*), 159(1). $^-BF_4$ is highly disordered and omitted for clarify.

(15) Motoyama, Y.; Narusawa, H.; Nishiyama, H. *Chem. Commun.* **1999**, 131.

Table 1. Asymmetric Alkylation of Imine 7 with R−Li[a]



7

10a: R = Me
10b: R = *n*-Bu

entry	complex	R	solvent	% yield	% ee[b]
1	3	Me	THF	54	68
2	4	Me	THF	58	71
3[c]	6	Me	THF	44	<2
4	3	Me	CH_2Cl_2	66	78
5	4	Me	CH_2Cl_2	71	78
6	3	*n*-Bu	CH_2Cl_2	72	82
7	4	*n*-Bu	CH_2Cl_2	88	81

[a] All reactions were carried out using 0.1 mmol of **5**, 0.1 mmol of Phebox complex **3** or **4**, and 0.3 mmol of RLi at −78 °C. [b] Determined by HPLC analysis using Daicel CHIRALCEL OD. [c] Complex **6** was prepared in situ from complex **5** with MeOTf.

aldimine would be the *trans* configuration.[16] While using the Pt(IV) complex **6**, the ^{1}H NMR spectrum showed free aldimine **7** and the starting complex **6**.

To determine the mode and magnitude of the asymmetric induction of these chiral aldimine complexes **8** and **9** generated in situ, asymmetric alkylation with organolithium reagents[17] was carried out. To a 1:1 mixture of the (*S*,*S*)-(Phebox)Pt(OTf) complex **3** and the aldimine **7** in tetrahydrofuran (THF) was added an ether solution of methyllithium (3 equiv) at −78 °C to produce the *N*-phenyl-1-phenylethylamine **10a** in 54% yield with 68% ee (Table 1, entry 1). The absolute configuration of **10a** proved to be *S* by comparison of the optical rotation with the literature value.[18] Using the [(Phebox)Pt(H_2O)](BF_4) complex **4**, almost the same result was obtained (entry 2). However, the (Phebox)-$PtCl_2$(OTf) complex **6** gave the racemic product (entry 3). The reaction in a dichloromethane solution made the enantiomeric excess increase to 78% ee for both complexes **3** and **4** (entries 4 and 5). Adoption of *n*-butyllithium eventually gave the corresponding amine **10b** in 81−82% ee (entries 6 and 7).

The observed absolute (*S*)-stereochemistry and higher enantioselectivity of the alkylated products using the (*S*,*S*)-Phebox−Pt complexes **3** and **4** (via **8** and **9**) can be unambiguously explained by the square planar Phebox−Pt−aldimine intermediate **A** (Figure 2). The C═N plane of the bound aldimine is perpendicular to the Phebox plane,[19] and the *re*-face of the imine is masked by one isopropyl substituent on the oxazoline rings. The organolithium reagents attacked the exposed

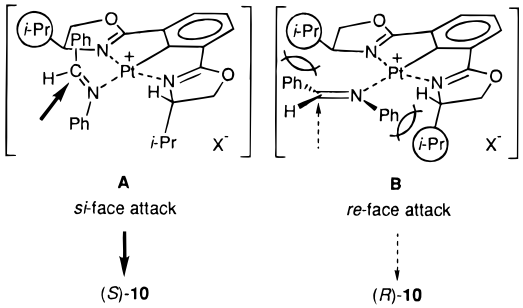
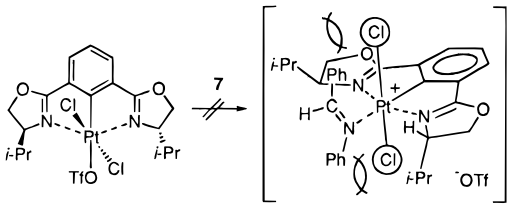


Figure 2.

Scheme 4



si-face of the bound aldimine, so the (*S*)-product was obtained. If the bound aldimine plane was placed almost parallel to the Phebox plane (**B**), which would be disfavored by steric repulsion between both phenyl substituents of the aldimine and the Phebox ligand, the opposite (*R*)-product would be obtained as the major enantiomer.

The resulting racemic product using the (Phebox)-$PtCl_2$(OTf) complex **6** was explained by the fact that the aldimine **7** cannot bind to the (Phebox)$PtCl_2$ fragments because of the steric repulsion between both phenyl substituents of aldimine and the chlorine atoms at the apical position on the Pt atom (Scheme 4, **C**). Therefore, the alkylation reaction occurred with the free aldimine, not the one bound to the chiral Phebox−Pt complex **6**, to produce the racemic product.

In conclusion, we have synthesized the Phebox−Pt complexes and have found that these complexes acted as efficient chiral assemblies[20] for the asymmetric alkylation of *N*-phenylbenzaldimine with organolithium reagents even in a stoichiometric manner. This finding can significantly provide important information about the steric course of the asymmetric alkyation of aldimines by Lewis acid coordination.

Experimental Section

General Methods. Anhydrous dichloromethane and tetrahydrofuran were purchased from Kanto Chemical Co. Silver

(16) Stark and Gladysz reported that the reaction of an aldimine [Ph(H)C═NMe] and the chiral CpRe(NO)(PPh_3)(OTf) complex gave kinetically the 95%-*cis* aldimine complex (Ph and Me substituents are *cis*), and then the *cis*/*trans* isomers slowly equilibrated in solution; see: Stark, G. A.; Gladysz, J. A. *Inorg. Chim. Acta* **1998**, *269*, 167.

(17) Asymmetric alkylation of aldimines. Reviews: (a) Tomioka, K. *Synthesis* **1990**, 541. Reference 1d. Recent representative papers: (b) Itsuno, S.; Yanaka, H.; Hachisuka, C.; Ito, K. *J. Chem. Soc., Parkin Trans. 1* **1991**, 1341. (c) Soai, K.; Hatanaka, T.; Miyazawa, T. *J. Chem. Soc., Chem. Commun*. **1992**, 1097. (d) Katrizky, A. R.; Harris, P. A. *Tetrahedron: Asymmetry* **1992**, *3*, 437. (e) Inoue, I.; Shindo, M.; Koga, K.; Tomioka, K. *Tetrahedron* **1994**, *50*, 4429. (f) Denmark, S. E.; Nakajima, N.; Nicaise, O. J.-C. *J. Am. Chem. Soc.* **1994**, *116*, 8797. Reference 16.

(18) (a) Wittig, G.; Thiele, U. *Justus Liebigs Ann. Chem*. **1969**, *726*, 1. (b) Landor, S. R.; Sonola, O. O.; Tatchell, A. R. *Bull. Chem. Soc. Jpn*. **1984**, *57*, 1658.

(19) This configuration would be electronically favored because the back-donation from the filled d_{xy} orbital of the platinum to the vacant p_x orbital of the aldimine's nitrogen readily makes a pπ−dπ interaction like (Pybox)$RuCl_2$(carbene) or (Pybox)$RuCl_2$(olefin) complexes [Pybox, 2,6-bis(oxazolinyl)pyridine]; see: (a) Nishiyama, H.; Aoki, K.; Itoh, H.; Iwamura, T.; Sakata, N.; Kurihara, O.; Motoyama, Y. *Chem. Lett*. **1996**, 1071. (b) Motoyama, Y.; Murata, K.; Kurihara, O.; Naitoh, T.; Aoki, K.; Nishiyama, H. *Organometallics* **1998**, *17*, 1251.

(20) Recent representative papers of chiral assemblies for asymmetric synthesis. 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*, 5, 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.

trifluoromethanesulfonate and silver tetrafluoroborate were purchased from Aldrich Chemical Co. ^{1}H and ^{13}C NMR spectra were measured on JEOL GNM-270 (270 MHz) spectrometers. Chemical shifts of ^{1}H NMR were described in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$) in $CDCl_3$, unless otherwise noted. Chemical shifts of ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard ($\delta = 77.1$), unless otherwise noted. IR spectra were measured on a JASCO FT/IR-230 spectrometer. Melting points were measured on a Yamato MP-21 and Yanaco MP-J3. Elemental analyses were measured on a Yanaco CHN CORDER MT-3. 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 column. Column chromatography was performed with silica gel (Merck, Art 7734). Analytical thin-layer chromatography (TLC) was performed on glass plates and aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F_{254}; layer thickness 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 nitrogen or argon atmosphere.

2,6-Bis(4′-(*S*)-isopropyloxazolin-2′-yl)phenyltrimethylstannane [(Phebox)SnMe$_3$]. (**1**) was prepared by our methods.[8a] $K[PtCl_3(C_2H_4)](H_2O)$ was prepared by the literature method.[21]

(Phebox)PtCl (2). To a suspended solution of $K[PtCl_3(C_2H_4)](H_2O)$ (200 mg, 0.48 mmol) in dichloromethane (7 mL) was added (Phebox)$SnMe_3$ (**1**) (223 mg, 0.48 mmol) at 0 °C. After stirring for 5 h at that temperature, the reaction mixture was concentrated under reduced pressure. Purification by silica gel chromatography (dichloromethane/methanol = 30:1) at 0 °C gave (Phebox)PtCl (**2**) in 88% yield (224 mg, 0.42 mmol) as yellow solids. Single crystals for the X-ray diffraction study were obtained from ethyl acetate at room temperature; decomp. 261−263 °C. IR (CH_2Cl_2): 2970, 1610, 1580, 1492, 1407, 1395, 1145, 960 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.80 (d, $J = 6.8$ Hz, 6H), 0.96 (d, $J = 6.8$ Hz, 6H), 2.90 (dsept, $J = 3.4$, 6.8 Hz, 2H), 4.40 (dt, $J = 3.4$, 7.8 Hz, 2H), 4.76 (d, $J = 7.8$ Hz, 4H), 7.18 (t, $J = 7.3$ Hz, 1H), 7.30 (d, $J = 7.3$ Hz, satellite $J_{Pt-H} = 8.3$ Hz, 2H). ^{13}C NMR (67.8 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. Calcd for $C_{18}H_{23}N_2O_2ClPt\cdot0.5H_2O$: C, 40.12; H, 4.49; N, 5.20%. Found: C, 40.32; H, 4.45; N, 5.33%.

(Phebox)Pt(OTf) (3). To a stirred solution of (Phebox)PtCl (**2**) (239 mg, 0.45 mmol) in dichloromethane (5 mL) was added silver triflate (150 mg, 0.59 mmol) at room temperature and stirred for 1 day. Then the reaction mixture was concentrated under reduced pressure. Purification by silica gel chromatography (dichloromethane/acetone = 5:1) gave (Phebox)Pt(OTf) (**3**) in 93% yield (269 mg, 0.42 mmol) as yellow solids; decomp. 223−224 °C. IR (KBr): 2975, 1610, 1550, 1490, 1390, 1280, 1250, 1040, 650 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.81 (d, $J = 6.8$ Hz, 6H), 0.97 (d, $J = 6.8$ Hz, 6H), 2.52 (dsept, $J = 6.8$, 3.4 Hz, 2H), 4.47 (ddd, $J = 8.8$, 6.8, 3.4 Hz, 2H), 4.77 (dt, $J = 8.8$ Hz, 2H), 4.82 (dd, $J = 8.8$, 6.8 Hz, 2H), 7.20 (t, $J = 8.3$ Hz, 1H), 7.34 (d, $J = 8.3$ Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 14.0, 18.4, 29.1, 66.8 (satellite, $J_{Pt-C} = 31.3$ Hz), 72.3 (satellite, $J_{Pt-C} = 27.4$ Hz), 120 0 (q, $J_{C-F} = 318.9$ Hz), 123.5, 127.8 (satellite, $J_{Pt-C} = 46.9$ Hz), 128.1 (satellite, $J_{Pt-C} = 40.1$ Hz), 151.0, 178.3 (satellite, $J_{Pt-C} = 213.2$ Hz). Anal. Calcd for $C_{19}H_{23}N_2O_5SF_3Pt\cdot CH_2Cl_2$: C, 32.98; H, 3.46; N, 3.85%. Found: C, 32.32; H, 3.45; N, 3.95%.

[(Phebox)Pt(H$_2$O)](BF$_4$) (4). To a stirred solution of (Phebox)PtCl (**2**) (100 mg, 0.189 mmol) in acetone (4.75 mL) and water (0.25 mL) was added silver tetrafluoroborate (110.2 mg, 0.566 mmol) at room temperature and stirred for 20 h. Then the reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. Recrystallization from acetone/benzene (1:1) gave [(Phebox)Pt(H_2O)](BF_4) (**4**) in 92% yield (102.9 mg, 0.172 mmol) as pale yellow solids. Single crystals for the X-ray diffraction study were obtained from benzene/acetone at room temperature; decomp. 197−199 °C. IR (KBr): 3401, 2960, 1612, 1582, 1490, 1407, 1127, 1063, 965, 738 cm^{-1}. ^{1}H NMR (270 MHz, CD_3OD): δ 0.80 (d, $J = 7.0$ Hz, 6H), 0.94(d, $J = 7.3$ Hz, 6H), 2.12 (m, 2H), 3.22 (s, 2H), 4.25 (m, 2H), 4.80−4.95 (m, 4H), 7.21(t, $J = 7.3$ Hz, 1H), 7.37(d, $J = 7.3$ Hz, 2H). ^{13}C NMR (67.8 MHz, CD_3OD): δ 14.5, 18.4, 31.2, 68.2 (satellite, $J_{Pt-C} = 31.3$ Hz), 73.8 (satellite, $J_{Pt-C} = 27.4$ Hz), 125.2, 128.8 (satellite, $J_{Pt-C} = 44.0$ Hz), 129.4, 152.8, 180.3. Anal. Calcd for $C_{18}H_{25}N_2O_3BF_4Pt\cdot0.5CH_2Cl_2$: C, 34.62; H, 4.08; N, 4.37%. Found: C, 34.12; H, 4.00; N, 4.42%.

(Phebox)PtCl$_3$ (5). To a stirred solution of (Phebox)PtCl (**2**) (293 mg, 0.55 mmol) in dichloroethane (40 mL) was added $CuCl_2(H_2O)_2$ (755 mg, 4.43 mmol) at room temperature. After stirring for 4 h at 40 °C, the reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. Purification by silica gel chromatography (dichloromethane/methanol = 30:1) at 0 °C gave (Phebox)$PtCl_3$ (**5**) in 99% yield as yellow solids; decomp. 133 °C. IR (KBr): 2925, 1614, 1493, 1415, 924, 737 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.99 (d, $J = 7.0$ Hz, 6H), 1.10 (d, $J = 7.0$ Hz, 6H), 3.03 (dsept, $J = 3.0$, 7.0 Hz, 2H), 4.57 (ddd, $J = 10.0$, 6.8, 3.0 Hz, 2H), 4.94 (dd, $J = 9.2$, 6.8 Hz, 2H), 5.01 (dd, $J = 10.0$, 9.2 Hz, 2H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.68 (d, $J = 7.6$ Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 14.8, 19.3, 28.1, 66.8 (satellite, $J_{Pt-C} = 19.5$ Hz), 73.1 (satellite, $J_{Pt-C} = 22.0$ Hz), 126.0 (satellite, $J_{Pt-C} = 8.5$ Hz), 126.8. 131.0 (satellite, $J_{Pt-C} = 23.2$ Hz), 158.7 (satellite, $J_{Pt-C} = 734.9$ Hz), 176.8. Anal. Calcd for $C_{18}H_{23}N_2O_2Cl_3Pt\cdot0.8CH_2Cl_2$: C, 33.76; H, 3.71; N, 4.19%. Found: C, 33.77; H, 3.70; N, 4.29%.

(Phebox)PtCl$_2$(OTf) (6). To a stirred solution of (Phebox)$PtCl_3$ (**5**) (51 mg, 0.083 mmol) in dichloroethane (5 mL) was added methyl triflate (47 mL, 0.416 mmol) and heated at 40 °C for 2 h under argon atmosphere. Then the reaction mixture was concentrated under reduced pressure to give (Phebox)$PtCl_2$(OTf) (**6**) which was used in the asymmetric alkylation of aldimine **7** without further purification. IR (KBr): 2964, 1615, 1496, 1420, 1259, 1031, 805, 642 cm^{-1}. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 0.96 (d, $J = 6.8$ Hz, 6H), 1.00 (d, $J = 7.6$ Hz, 6H), 2.64 (m, 2H), 4.70 (m, 2H), 4.94−5.13 (m, 4H), 7.50−7.78 (m, 3H).

General Procedure for the Asymmetric Alkylation of Aldimine 7 with Organolithium Reagents Using Phebox−Platinum Complexes. To a stirred solution of Phebox−Pt complex (0.1 mmol) in THF (1 mL) was added imine **7** (0.1 mmol), and the mixture was stirred for 1 h at room temperature. After concentration under reduced pressure, the imine complex was obtained. To a stirred solution of imine complex in dichloromethane (1 mL) was added organolithium reagent (0.3 mmol) at −78 °C. After stirring for 1 h at that temperature, the reaction mixture was quenched by the addition of saturated NH_4Cl and extracted with dichloromethane. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Purification by silica gel chromatography gave product.

***N*-Phenyl-α-methylbenzenemethaneamine (10a).** $[\alpha]_D^{20}$ −2.4° (c 0.88, $CHCl_3$), (68% ee, *S*); lit.[18b] $[\alpha]_D^{20}$ −6.2° (c 50, $CHCl_3$). IR (neat): 3410, 3030, 2971, 1602, 1502, 1314, 1087, 752, 696 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.52 (d, $J = 6.4$ Hz, 3H), 4.02 (bs, 1H), 4.49 (d, $J = 6.4$ Hz, 1H), 6.52 (dd, $J = 8.8$, 1 0 Hz, 2H), 6.64 (dt, $J = 1.0$, 6.8 Hz, 1H), 7.09 (dd, $J = 8.8$, 6.8 Hz, 2H), 7.22−7.40 (m, 5H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 25.0, 53.5, 113.3, 117.2, 125.8, 126.8, 128.6, 129.1, 145.2, 147.3. Daicel CHIRALCEL OD, UV detector 254 nm, hexane/*i*-PrOH = 9:1; flow rate, 0.5 mL/min. $t_R = 12.4$ min (*R*), 15.3 min (*S*).

(21) Chatt, J.; Searle, M. L. *Inorg. Chem.* **1957**, *5*, 210.

***N*-Phenyl-α-butylbenzenemethaneamine (10b).** $[\alpha]_D^{20}$ +27.5° (c 0.87, $CHCl_3$), (82% ee); lit.[22] $[\alpha]_D^{25}$ +2.72° (c 1.14, MeOH), (65% ee). IR (neat): 3413, 3026, 2929, 2862, 1601, 1501, 1456, 1315, 1085, 750, 696 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 0.89 (t, J = 8.1 Hz, 3H), 1.26−1.40 (m, 4H), 1.79 (m, 2H), 4.06 (d, J = 6.4 Hz, 1H), 4.29 (dt, J = 6.5, 6.4 Hz, 1H), 6.51 (dd, J = 8.2, 1 0 Hz, 2H), 6.62 (dt, J = 1.0, 7.3 Hz, 1H), 7.06 (dd, J = 8.2, 7.3 Hz, 2H), 7.05−7.33 (m, 5H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 13.9, 22.6, 28.5, 38.7, 58.2, 113.2, 117.1, 126.4, 126.8, 128.5, 129.1, 144.4, 147.5. Daicel CHIRALCEL OD, UV detector 254 nm, hexane/*i*-PrOH = 9:1; flow rate, 0.5 mL/min. t_R = 9.0 min (minor), 10.5 min (major).

NMR Studies of the Complexation of Phebox−Platinum Complexes with *N*-Phenylbenzaldimine. To a stirred solution of Phebox−Pt complex **3** or **4** (0.05 mmol) in THF (2 mL) was added *N*-phenylbenzaldimine **7** (9.1 mg, 0.05 mmol) at room temperature under an argon atmosphere. After stirring for 1 h at room temperature, the resultant mitxure was concentrated under reduced pressure. The solid residue was dissolved in $CDCl_3$; then the resultant solution was placed with a syringe in a well-dried 5 mm NMR tube replaced by argon. All FID collections at the appropriate timing were stored on a floppy diskette.

[(Phebox)Pt(*N*-phenylbenzaldimine)]X (X = OTf, BF_4) (8 and 9). ^1H NMR (270 MHz, $CDCl_3$): δ 0.65 (d, J = 6.8 Hz, 3H), 0.72 (d, J = 7.3 Hz, 3H), 0.75 (d, J = 7.3 Hz, 3H), 0.76 (d, J = 6.8 Hz, 3H), 1.55−1.75 (m, 2H), 2.61 (m, 1H), 2.91 (m, 1H), 4.45 (t, J = 9.8 Hz, 1H), 4.56 (dd, J = 9.8, 6,4 Hz, 3H), 4.55−4.70 (m, 2H), 7.31 (t, J = 8.3 Hz, 1H), 7.40−7.65 (m, 7H), 7.69−7.80 (m, 3H), 8.07 (d, J = 8.3 Hz, 2H), 9.53 (satellite, J_{Pt-H} = 51.3 Hz).

X-ray Structure Determination and Details of Refinement. X-ray-quality crystals of **2** and **4** were obtained directly from the preparations described above and mounted in a glass capillary. Diffraction experiments were performed on a Rigaku AFC-7R four-circle diffractometer equipped with graphite-monochromated Mo K*a* radiation, λ = 0.710 69 Å. The lattice parameters and orientation matrixes were obtained and refined from 25 machine-centered reflections with 31.20 < 2θ < 37.35° for **2** and from 24 machine-centered reflections with 29.06 < 2θ < 29.93° for **4**. Intensity data were collected using a ω−2θ 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 2.

The structure was solved by heavy-atom Patterson methods[23] and expanded using Fourier techniques.[24] The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1946 observed reflections ($I > 3\sigma(I)$) and 216 variable parameters for **2** and was based on 1118 observed reflections ($I > 3\sigma(I)$) and 116 variable parameters for **4**. Neutral atom scattering factors were taken from Cromer and Waber.[25] All calculations were performed using the teXsan[26] crystallographic software package. Final refinement details are collected in Table 2, and the numbering schemes employed are shown in Figure 1, which were drawn with ORTEP at 30% probability ellipsoid.

Table 2. Crystallographic Data and Structure Refinement for Complexes 2 and 4

formula	$C_{18}H_{23}N_2O_2ClPt$	$C_{18}H_{23}N_2O_3BF_4Pt$
fw	529.93	599.30
cryst syst	monoclinic	orthorhombic
space group	$P2_1$	$P2_12_12$
cell constants		
a, Å	6.407(2)	14.698(4)
b, Å	11.7736(8)	6.084(3)
c, Å	12.415(2)	11.752(4)
β, deg	104.06(1)	
V, Å^3	908.4(2)	1050(1)
Z value	2	2
D_{calcd}, g cm^{-3}	1.937	1.894
F(000)	512	580
μ(Mo Kα), cm^{-1}	78.52	67.05
radiation; λ, Å	Mo Kα; 0.710 69	Mo Kα; 0.710 69
temp, °C	20.0	23.0
$2\theta_{max}$, deg	55.1	55.0
scan type	ω-2θ	ω-2θ
scan width (in ω)	1.00° + 0.30° tan θ	1.15° + 0.30° tan θ
no. of total data collcd	2407	1429
no. of unique data	2219 (R_{int} = 0.048)	
no. of obsd rflcns	1946 ($I > 3\sigma$)	1118 ($I > 3\sigma$)
no. of variables	216	116
residuals: *R*; R_w	0.026; 0.033	0.054; 0.083

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

Supporting Information Available: Text describing the synthesis of (Phebox)$SnMe_3$ (**1**) and tables of crystal structure parameters and details of data collection, bond angles and distances, and atomic positional and thermal parameters of **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990251K

(22) Nakagawa, M.; Kawata, T.; Kakikawa, T.; Yamada, H.; Matsui, T.; Hino, T. *Tetrahedron* **1993**, *49*, 1739.
(23) Fan, H.-F. *SAPI91: Structure Analysis Programs with Intelligent Control*; Rigaku Corp.: Tokyo, Japan, 1991.
(24) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *DIRDIF92*: *The DIRDIF program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.
(25) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.
(26) *teXane: Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.