Chiral Ruthenium−Bis(oxazolinyl)pyridine Complexes of α,β-Unsaturated Carbonyl Compounds: Enantioface-Selective Coordination of Olefins

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The reaction of $[(p\text{-cymene})RuCl_2]_2$ and 2,6-bis(oxazolinyl)pyridines (Pybox; **1**) in the presence of α,β-unsaturated carbonyl compounds as prochiral olefins gave η^2-olefin complexes. On the basis of NOE measurements and X-ray structural studies of (Ph-Pybox)$RuCl_2$(methyl acrylate) (**8a**) and (Me-Pybox)$RuCl_2$(acrolein) (**10b**) complexes, we revealed that the chiral (*S*,*S*)-(Pybox)$RuCl_2$ fragments are differentiated with regard to the one enantioface (*si* face) of the olefins, fixing the carbonyl moieties in an *s-trans* conformation. X-ray diffraction of the nonsubstituted (dH-Pybox)$RuCl_2$(acrolein) (**10d**) indicated that the preferential *s-trans* arrangements of α,β-unsaturated carbonyl compounds bound to the (Pybox)$RuCl_2$ fragments are not due to the substituents on the Pybox ligands but to the octahedral structures of the (Pybox)$RuCl_2$(olefin) complexes, especially affected by the chlorine atoms at the apical positions on the ruthenium atom. We also found that the (Pybox)$RuCl_2$ fragments act as efficient chiral assemblies for the asymmetric alkylation of the coordinated acrolein with phenyllithium, resulting in 87% ee of the corresponding alcohol **11**.

Introduction

Transition-metal η^2-olefin complexes[1] have been extensively studied in terms of not only structural characterization and bonding properties[2] but also model simulations in catalytic reactions.[3] Especially, chiral metal−olefin complexes[4−6] have been recognized to offer a variety of potential applications in asymmetric synthesis. Therefore, it is of importance to clarify the behavior of bound olefins in coordination spheres. Although there have been many reports on discrimination of an enantioface of simple olefins such as styrene or propylene by chiral transition-metal complexes,[5] multifunctionalized-olefin complexes have not been studied nearly as much to date.[6] Among such multifunctionalized olefins, α,β-unsaturated carbonyl compounds[7] commonly connect to traditional Lewis acids such as the typical or early-transition-metal compounds to form corresponding C=O/σ type bonds toward the metal centers.[8] On the other hand, late-transition-metal complexes mainly bind α,β-unsaturated carbonyl compounds through their C=C/π bonds. In this context, strongly cationic transition-metal complexes, such as the chiral rhenium complexes developed by Gladysz, can also capture the carbonyl groups just as common Lewis acids (Figure 1).[6b] Such transition-metal Lewis acid

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(3) Collman, J. P. *Acc. Chem. Res.* **1968**, *1*, 136 and references therein.

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(6) Recent representative papers are as follows. α,β-Unsaturated carbonyl compounds: (a) Kegley, S. E.; Walter, K. A.; Bergstrom, D. T.; MacFarland, D. K.; Young, B. G.; Rheingold, A. L. *Organometallics* **1993**, *12*, 2339. (b) Wang, Y.; Agbossou, F.; Dalton, D. M.; Liu, Y.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2699. (c) Schmid, G.; Kilanowski, B.; Boese, R.; Bläser, D. *Chem. Ber.* **1993**, *126*, 899. (d) Ferrara, M. L.; Orabona, I.; Ruffo, F.; Funicello, M.; Panunzi, A. *Organometallics* **1998**, *17*, 3832. Other substituted olefins: (e) Jedlicka, B.; Rülke, R. E.; Weissensteiner, W.; Fernandez-Galan, R.; Jalon, F. A.; Manzano, B. R.; Rodriguez-de la Fuente, J.; Veldman, N.; Kooijman, H.; Spek, A. L. *J. Organomet. Chem.* **1996**, *516*, 97. (f) Erickson, L. E.; Hayes, P.; Hooper, J. J.; Morris, K. F.; Newbrough, K. F.; van Os, M.; Slangen, P. *Inorg. Chem.* **1997**, *36*, 284. (g) Selvakumar, K.; Valentini, M.; Wörle, M.; Pregosin, P. S.; Albinati, A. *Organometallics* **1999**, *18*, 1207.

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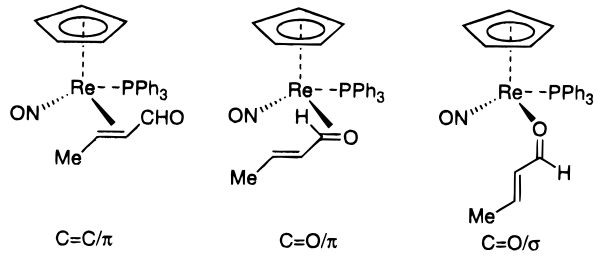


Figure 1. C═C/π, C═O/π, and C═C/σ structures of CpRe(NO)(PPh_3)(crotonaldehyde) complexes.

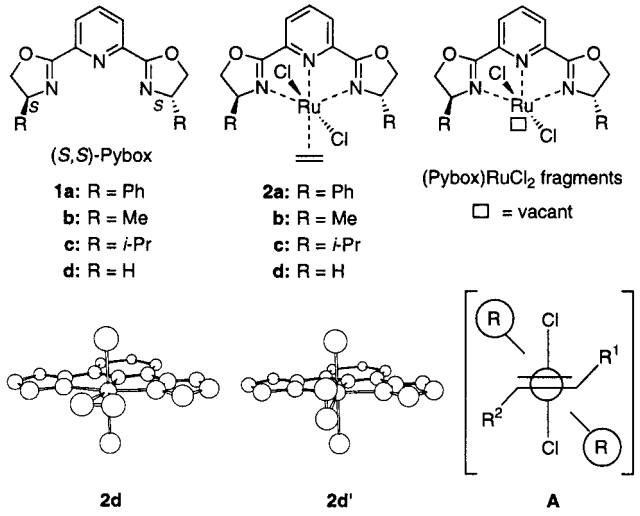
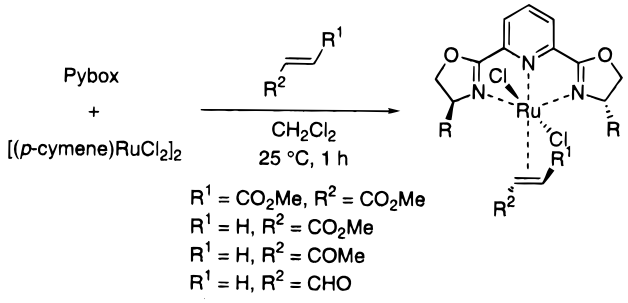


Figure 2.

complexes have recently been applied to asymmetric catalytic reactions.[9] In this situation, study of the coordination mode of α,β-unsaturated carbonyl compounds in chiral circumstances provides very important information for creating new reaction systems and elucidating reaction mechanisms.

We have previously reported that C_2-symmetric 2,6-bis(oxazolin-2-yl)pyridines (Pybox; **1**) are effective ligands for Ru(II)-catalyzed asymmetric cyclopropanation.[10] During the course of our studies on Ru-catalyzed cyclopropanation systems, in which chiral ethylene complexes **2** were used as catalyst precursors, we successfully clarified the structure of the nonchiral dihydro-Pybox (dH-Pybox) derived ethylene complex **2d** by X-ray analysis.[10b] The ethylene moiety on **2d** is coordinated parallel to the Pybox plane and perpendicular to the Cl−Ru−Cl plane. Extended Hückel molecular orbital (EHMO) calculations on (dH-Pybox)$RuCl_2$(C_2H_4-0°) (**2d**) and (dH-Pybox)$RuCl_2$(C_2H_4-90°) (**2d′**) were carried out, showing that isomer **2d** was more stable than **2d′** by 1.48 eV (34.2 kcal/mol). This result suggests that one enantioface (the *si* face) of substituted olefins could be differentiated by binding it to this Pybox−ruthenium (Pybox-Ru) fragment (**A**; Figure 2). Here we describe in full detail[11] the characterization of the chiral (Pybox)-$RuCl_2$ complexes of α,β-unsaturated carbonyl compounds by X-ray diffraction and NMR studies including VT, NOE, and J_{C-H} measurements (Scheme 1). Furthermore, the asymmetric alkylation reaction of acrolein bound to the (Pybox)$RuCl_2$ fragments was demonstrated with phenyllithium and phenylmagnesium reagents.

Scheme 1



Results and Discussion

1,2-Disubstituted Olefin Complexes. First, we adopted dimethyl fumarate (*trans*-ZCH═CHZ, Z = CO_2Me) as a *trans*-1,2-disubstituted olefin and synthesized the corresponding complex (**3a**) derived from Ph-Pybox (**1a**). To a solution of [(*p*-cymene)$RuCl_2$]$_2$ and dimethyl fumarate (2 equiv) in dichloromethane was added Ph-Pybox (**1a**), and the mixture was stirred for 1 h at 25 °C under an argon atmosphere. After the solvent was removed under reduced pressure, the residue was washed with ether−hexane (ca. 1:1) to remove an excess of the olefin and dissociated *p*-cymene. The dark brown solid product **3a** was obtained in 78% yield. The ^{1}H and ^{13}C NMR spectra of the product **3a** showed a C_2-symmetric structure. The signals of olefinic protons and carbons of coordinated dimethyl fumarate appear at higher field than the uncomplexed (free) one (from δ 6.87 to 5.64 ppm in ^{1}H NMR and from δ 133.1 to 69.4 ppm in ^{13}C NMR). These results indicated that dimethyl fumarate is coordinated to the (Ph-Pybox)$RuCl_2$ fragment by the C═C bond; i.e., **3a** is a η^2-olefin complex. Even at a lower temperature (ca. −80 °C), the complex **3a** was the sole product observed. From the NOE spectra of the complex **3a**, 4−7% NOEs were observed between the olefinic proton H_a of the fumarate and the aromatic protons of the phenyl substituents on the oxazoline rings of the Pybox ligand, while no NOE was observed between H_a and H_N (Figure 3).[12] These NOE experiments and the results of parallel coordination of olefins to the Pybox plane by EHMO calculation result

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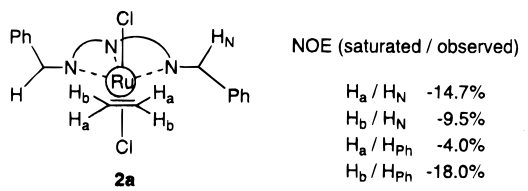
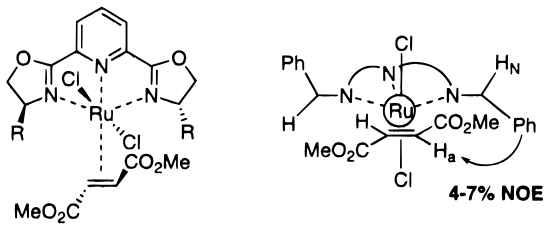
(11) Our preliminary communication: (a) Motoyama, Y.; Murata, K.; Kurihara, O.; Naitoh, T.; Aoki, K.; Nishiyama, H. *Organometallics* **1998**, *17*, 1251. Recently, we reported the kinetic resolution of a recemic *trans*-cyclooctene by discriminative coordination with the chiral (Pybox)$RuCl_2$ fragments; see: (b) Nishiyama, H.; Naitoh, T.; Motoyama, Y.; Aoki, K. *Chem. Eur. J.* **1999**, *5*, 3509.

(12) At the ethylene complex **2a**, the NOE between H_a and H_N was stronger than that between H_b and H_N. Furthermore, a strong −18.0% NOE was observed between H_b and the aromatic protons (H_{Ph}) of the phenyl substituents on the oxazoline rings of the Pybox ligand.

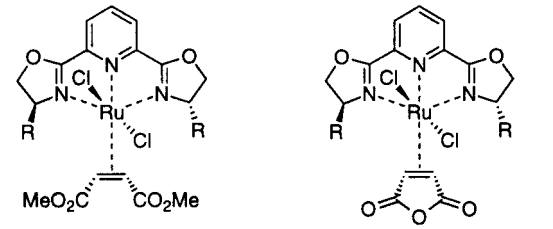




3a: R = Ph
b: R = Me
c: R = *i*-Pr

3a

Figure 3.



4a : R = Ph
4c : R = *i*-Pr

5a : R = Ph
5b : R = Me

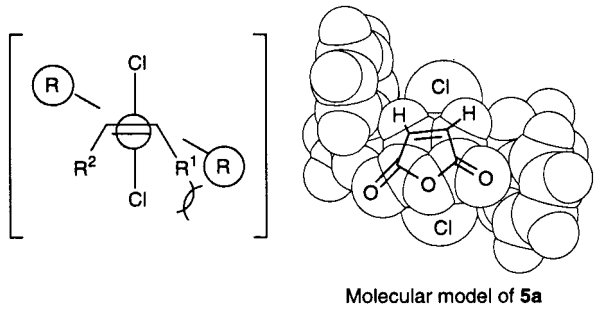
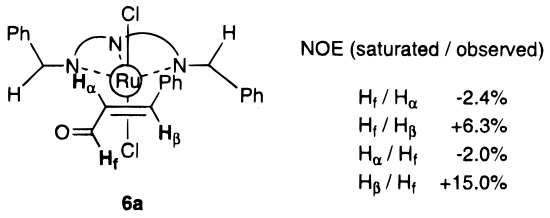


Figure 4.

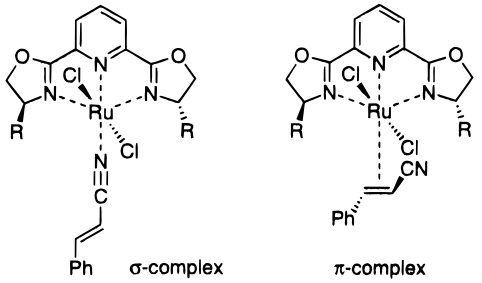
in the conclusion that one enantioface (*si*,*si* face) of the olefin moiety can be differentiated by using (*S*,*S*)-Pybox. In addition, this chiral (Ph-Pybox)$RuCl_2$ fragment fixes the conformation of the carbonyl moiety as either *s-cis* or *s-trans*. Furthermore, the preferential discrimination of the π-enantioface of fumarate is independent of the substituents (Ph, Me, or *i*-Pr) on the Pybox ligands **1**. Even the Me group, which is the smallest substituent, can select the *si*,*si* face of fumarate perfectly. These fumarate complexes **3a**−**c** could not be isolated in pure form because of gradual dissociation of the bound fumarate in solution: stability **3a** > **3b**,**c**.

Second, we carried out the reaction with dimethyl maleate (*cis*-ZCH=CHZ, Z = CO_2Me) and maleic anhydride (OC(O)CH=CHCO) as 1,2-*cis*-substituted olefins. Dimethyl maleate gave the corresponding ruthenium complexes **4a**,**c** with Ph-Pybox **1a** and *i*-Pr-Pybox **1c**, respectively. These complexes **4a**,**c** are less stable than the fumarate complexes **3a**−**c**. They readily released dimethyl maleate in dichloromethane or chloroform (decomposition rate 50%, ca. 0.5 h). This fact can probably be accounted for by the steric repulsion between one ester group of maleate and one substituent on the oxazoline rings. In contrast, the maleic anhydride complexes **5a**,**b**, which were obtained by a similar method, proved to be stable enough to be isolated on a silica gel column at 0 °C (85% for **5a** and 63% for **5b**) (Figure 4). On the basis of the van der Waals model of



6a

Figure 5.



7a : R = Ph
7c : R = *i*-Pr

Figure 6.

5a, maleic anhydride can likely fit in the vacant site of the (Ph-Pybox)$RuCl_2$ fragment.

Next, we chose methyl cinnamate (*trans*-PhCH=$CHCO_2Me$) and cinnamaldehyde (*trans*-PhCH=CHCHO) as olefin candidates. Although methyl cinnamate could not bind to the (Pybox)$RuCl_2$ fragments, sterically less hindered cinnamaldehyde formed the corresponding η^2-olefin complex **6a** with a single conformation in solution using Ph-Pybox (**1a**). Irradiation of the formyl proton (H_f) resulted in a 6.3% NOE to the β-proton (H_β) and −2.4% NOE to the α-proton (H_α). However, strong 15.0% NOE was observed between H_β and H_f (Figure 5). Therefore, it can be concluded that the conformation of the bound cinnamaldehyde is *s-trans*. In contrast, crotonaldehyde (*trans*-CH_3CH=CHCHO) failed to produce a stable complex.

As an α,β-unsaturated nitrile, cinnamonitrile (*trans*-PhCH=CHCN) was then examined to show that the nitrile's nitrogen atom exclusively makes σ-complexes with the (Pybox)$RuCl_2$ fragments (Figure 6). From the ^{13}C NMR spectra of **7a**,**c**, the signals of olefinic carbons of the bound cinnamonitrile appear at slightly lower field than the unbound ones: δ 130.3 (C_α) and 149.3 (C_β) ppm for free cinnamonitrile, δ 130.8 (C_α) and 150.1 (C_β) ppm for **7a**, and δ 131.2 (C_α) and 149.3 (C_β) ppm for **7c**, respectively. The ^1H NMR spectrum of **7c** shows that the signals of olefinic protons of the bound cinnamonitrile appear at lower field than those of the unbound one; from δ 5.88 to 6.47 ppm for the α-proton (H_α) and from δ 7.40 to 7.50 ppm for the β-proton (H_β). However, higher field shifts are observed at the olefinic proton of **7a** (δ 4.56 for H_α and 6.50 ppm for H_β). The observed high-field shift of the olefinic protons of cinnamonitrile on **7a** was thought to be a shielding effect by the phenyl ring on the oxazoline rings. These σ-nitrile complexes **7a**,**c** were stable enough to be purified by chromatography at 0 °C in 99% and 92% yields, respectively.

Monosubstituted Olefin Complexes. The other (Pybox-Ru)(olefin) complexes **8a**−**c**, **9a**−**c**, and **10a**−**d** with monosubstituted α,β-unsaturated carbonyl com-

Table 1. Preparation of α,β-Unsaturated Carbonyl Compounds-Coordinated Pybox-Ru Complexes[a]

entry	olefin	Pybox	complex	% yield[b]
1	MeO_2C	**1a**	**8a**	86
2		**1b**	**8b**	83
3		**1c**	**8c**	(87)[c]
4	Me(O)C	**1a**	**9a**	95
5		**1b**	**9b**	92
6		**1c**	**9c**	(78)[c]
7	OHC	**1a**	**10a**	93
8		**1b**	**10b**	96
9		**1c**	**10c**	91
10		**1d**	**10d**	96

[a] All reactions were carried out using 2 equiv of Pybox and 4 equiv of olefin based on $[(p\text{-cymene})RuCl_2]_2$ for 1 h under an argon atmosphere at 25 °C. [b] Isolated yield by silica gel chromatography at −60 °C. [c] Based on ^1H NMR.

pounds, such as methyl acrylate, methyl vinyl ketone, and acrolein, have been synthesized and characterized in a similar manner (Table 1). In all of the experiments, the ^1H and ^{13}C NMR spectra of the products **8**−**10**, with a single set of diastereotopic vinylic proton and carbon resonances present in variable-temperature (VT) measurements (−80 to +25 °C), provide strong evidence for the exclusive binding of one enantioface of the olefins to the chiral (Pybox)$RuCl_2$ fragments. These results imply that these (*S*,*S*)-(Pybox)$RuCl_2$ fragments not only differentiate the *si* enantioface of the olefins but also fix the conformation of the carbonyl moieties *s-trans*, similarly to the cinnamaldehyde complex **6a**. The complexes **8a**,**b**, **9a**,**b**, and **10a**,**b** derived from Ph-Pybox (**1a**) and Me-Pybox (**1b**) could be isolated by silica gel column chromatography at −60 °C. With *i*-Pr-Pybox (**1c**), the acrolein complex **10c** could only be isolated. Similarly, dissociation of methyl acrylate, methyl vinyl ketone, and acrolein were observed for **8a**−**c**, **9a**−**c**, and **10a**−**c** in solution ($CDCl_3$) at 25 °C; dissociation rate ca. 50−70%, 7 h. However, acrolein on **10d** with dH-Pybox (**1d**) did not dissociate.

The (Ph-Pybox)$RuCl_2$(η^2-methyl acrylate) complex **8a** was eventually characterized by a single-crystal X-ray diffraction (Figure 7).[13] Table 2 lists some of the relevant bond distances and angles. The coordination geometry around the ruthenium atom is slightly distorted octahedral. The angle N(2)−Ru(1)−N(3) is 153.7°. The C═C moiety of the acrylate, coordinated by the *si* face, is placed in parallel to the Pybox plane (ca. 2−8°). The bond length of C(24)−C(25) is 1.41 Å. The carbonyl group of the acrylate is *s-trans* toward the C═C bond. The torsion angle O(3)−C(16)−C(15)−C(14) is 169°. The O(3)−C(26)−O(4)−C(27) angle is 9°, and the ester methyl group is located in the C═C−C═O plane in a *syn* configuration to the carbonyl oxygen atom.

The parallel coordination of the C═C bond to the Pybox plane can be elucidated by back-donation of electrons of the filled d orbital in the Pybox plane to the vacant p orbital of the coordinated carbons C(24) and C(25). According to the *ab initio* calculations of free (uncoordinated) methyl acrylate, the *s-cis*/*syn* conformer is more stable than the *s-trans*/*syn* structure at the 3-21G level.[14] In fact, Ruffo et al. clarified that the conformation of acrylate of [(*N*,*N*-chelate)Pt(Me)] (*N*,*N*-chelate = diacetyl bis(diethylphenylimine)) fragment **B** is *s-cis*/*syn* by X-ray diffraction (Figure 8).[15a] However, the *s-cis*/*s-trans* configuration is highly dependent on the structure of the metal fragment. X-ray analysis of (dmphen)PtCl($SnMe_2Cl$)(η^2-dimethyl fumarate) (dmphen = 2,9-dimethyl-1,10-phenanthroline) complex **C** showed that the conformation of the CO_2Me group facing the chloride is *s-trans*. Another ester moiety, facing the stannyl group, is arranged in an *s-cis* fashion because of the strong interaction between the carbonyl oxygen atom and the tin atom (Sn−O 2.677 Å). In contrast,

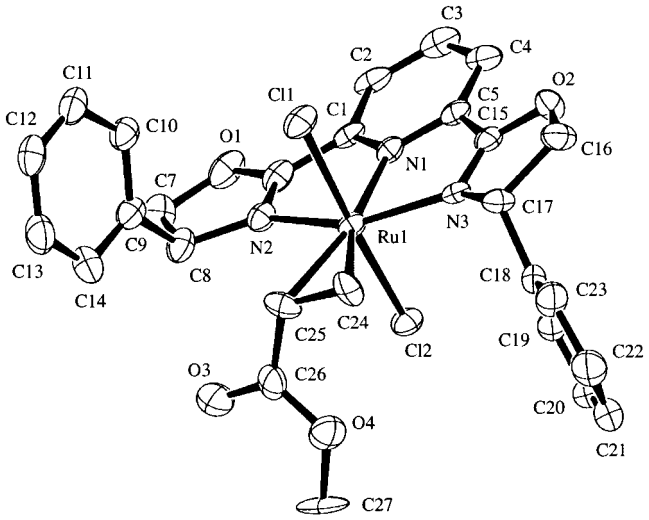


Figure 7. Molecular structure of (Ph-Pybox)$RuCl_2$(η^2-methyl acrylate) (**8a**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for (Ph-Pybox)$RuCl_2$(η^2-methyl acrylate) (8a)

Ru(1)−Cl(1)	2.381(3)	Ru(1)−Cl(2)	2.398(3)
Ru(1)−N(1)	2.008(8)	Ru(1)−N(2)	2.128(8)
Ru(1)−N(3)	2.085(9)	Ru(1)−C(24)	2.219(10)
Ru(1)−C(25)	2.22(1)	O(1)−C(6)	1.33(1)
O(1)−C(7)	1.47(1)	O(2)−C(15)	1.34(1)
O(2)−C(16)	1.48(1)	O(3)−C(26)	1.22(1)
O(4)−C(26)	1.35(1)	O(4)−C(27)	1.48(1)
N(1)−C(1)	1.35(1)	N(1)−C(5)	1.35(1)
N(2)−C(6)	1.28(1)	N(2)−C(8)	1.51(1)
N(3)−C(15)	1.28(1)	N(3)−C(17)	1.49(1)
C(24)−C(25)	1.41(1)		

Cl(1)−Ru(1)−Cl(2)	175.6(1)	Cl(1)−Ru(1)−N(1)	88.5(2)
Cl(1)−Ru(1)−N(2)	89.9(2)	Cl(1)−Ru(1)−N(3)	86.4(2)
Cl(1)−Ru(1)−C(24)	85.8(3)	Cl(1)−Ru(1)−C(25)	89.7(3)
Cl(2)−Ru(1)−N(1)	87.0(2)	Cl(2)−Ru(1)−N(2)	89.1(2)
Cl(2)−Ru(1)−N(3)	92.7(2)	Cl(2)−Ru(1)−C(24)	98.3(3)
Cl(2)−Ru(1)−C(25)	94.5(3)	N(1)−Ru(1)−N(2)	76.9(3)
N(1)−Ru(1)−N(3)	77.0(3)	N(1)−Ru(1)−C(24)	157.2(4)
N(1)−Ru(1)−C(25)	165.2(4)	N(2)−Ru(1)−N(3)	153.7(3)
N(2)−Ru(1)−C(24)	125.1(4)	N(2)−Ru(1)−C(25)	88.5(4)
N(3)−Ru(1)−C(24)	80.5(4)	N(3)−Ru(1)−C(25)	117.5(4)
C(24)−Ru(1)−C(25)	37.0(4)	C(6)−O(1)−C(7)	107.4(9)
C(15)−O(2)−C(16)	105.4(9)	C(26)−O(4)−C(27)	117(1)
C(6)−N(2)−C(8)	108.3(9)	C(15)−N(3)−C(17)	106.4(9)

(13) These crystals were obtained from the mixture of (*S*,*S*)- and (*R*,*R*)-**8a**; there are two independent molecules of (*S*,*S*)- and (*R*,*R*)-**8a** in the unit cell.

(14) Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14.
(15) (a) Ganis, P.; Orabona, I.; Ruffo, F.; Vitagliano, A. *Organometallics* **1998**, *17*, 2646. (b) Albano, V. G.; Castellari, C.; Monari, M.; De Felice, V.; Panunzi, A.; Ruffo, F. *Organometallics* **1996**, *15*, 4012.

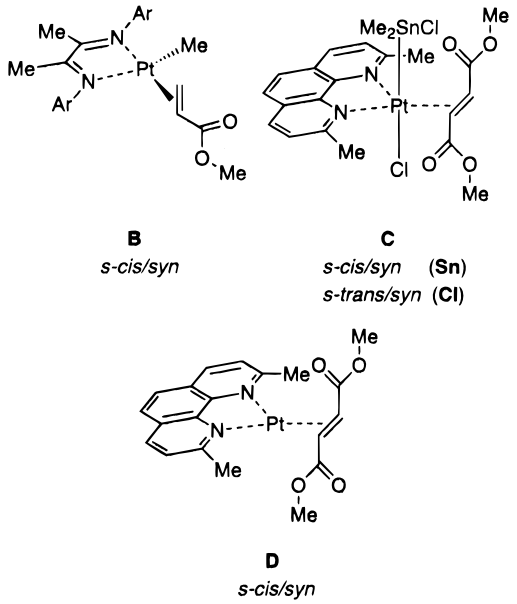


Figure 8.

(dmphen)Pt(η^2-dimethyl fumarate) complex **D**, without apical chloride as in **C**, maintains dimethyl fumarate in an *s-cis* conformation.[15b] In comparison to these platinum complexes, the *s-trans* conformation of the bound acrylate of the (Pybox)$RuCl_2$ complexes can be considered as a result of the steric and/or dipolar repulsion between the carbonyl oxygen atom and the chlorine atoms at the apical position. Therefore, the carbonyl moiety of the fumarate on **3a** may be an *s-trans/syn* arrangement, similarly.

We also characterized the structures of the acrolein complexes **10b** (R = Me) and **10d** (R = H) by X-ray diffraction. The ORTEP drawings are shown in Figure 9, and the selected bond distances and angles are summarized in Tables 3 and 4, respectively. The C=C moiety of acrolein on **10b** is coordinated by the *si* face and is parallel to the Pybox plane (ca. 4−8°) in a manner similar to that for the acrylate complex **8a**. The Ru−C_β (C_β = β-carbon of acrolein) bonds are shorter than the Ru−C_α (C_α = α-carbon of acrolein) bonds; the Ru−C_β distance is 2.20 Å for both **10b** and **10d**, and Ru−C_α distances are 2.24 and 2.27 Å for **10b**,**d**, respectively. The conformation of the carbonyl moieties of both complexes **10b**,**d** is *s-trans*; the torsion angle O(3)−C(16)−C(15)−C(14) of **10b** is 169°, and O(3)−C(14)−C(13)−C(12) of **10d** is 167°.

Behavior of Monosubstituted Olefin Complexes in Solution. While the signals of the both olefinic carbons (C_α and C_β) of **10b** and **10d** appear at higher field (ca. 60 ppm) than those of the uncomplexed ones, the signals of their formyl carbons (C_f) shift to lower field (∼15 ppm) in ^{13}C NMR. Therefore, we tried to examine the hybridization character of both the olefinic carbons (C_α and C_β) and the formyl carbon (C_f) of the acrolein on the basis of the J_{C-H} coupling constants by nondecoupling ^{13}C NMR spectroscopy at 25 °C. The J_{C-H} coupling constants of free acrolein were 161.1 Hz for C_α, 164.8 Hz for C_β, and 173.3 Hz for C_f (Table 5, entry 1). The J_{C-H} coupling constants of C_f on the ruthenium were increased: 184.3 Hz for **10b** and 188.9 Hz for **10d**. These data can account for the decrease in conjugation of the formyl group of the coordinated acrolein. While the coupling constants of C_α are slightly increased (2.5 Hz), those of C_β decrease remarkably to 155−156 Hz for both **10b** and **10d**. It is clear that the C_β atom obtains more sp^3 character than the C_α atom by coordination.

Next, we measured difference NOE of the monosubstituted olefin complexes **8**−**10** to study the structures around the C−C single bonds between C_α and C(=O). However, no NOEs were obtained for the corresponding protons of the methyl ester group on **8** or the methyl group on **9** toward both C_α and C_β protons, respectively. The NOE spectrum of the acrolein on **10c** (R = *i*-Pr) showed a 7% NOE to $H_{\beta t}$ and no NOE to H_α by irradiation of H_f (Table 6). Irradiation of $H_{\beta t}$ again led to a strong 12% NOE to H_f. For **10b**,**d**, strong 13% and 16% NOEs were observed between H_f and $H_{\beta t}$, respectively. The J_{C-H} experiments suggested that the CHO groups can rotate between C_α and C_f because of decreasing delocalization at the C=C−C=O moieties; however, these NOE results can be considered as indicative that the conformation of the coordinated acroleins is mainly an *s-trans* arrangement on the NMR time scale, as for the X-ray crystal structures.

Asymmetric Phenylation of Chiral Acrolein Complexes 10. We have endeavored to evaluate the magnitude of asymmetric induction with these chiral (Pybox)-$RuCl_2$ fragments as chiral assemblies.[16] Therefore, asymmetric phenylation of the formyl groups of the corresponding complexes **10a**−**c** with phenyllithium and phenylmagnesium bromide[17] was examined. A solution of the (*S*,*S*)-(Ph-Pybox)$RuCl_2$(acrolein) complex **10a** in THF was treated with an ether solution of phenyllithium (2 equiv) at −78 °C to give the 1,2-addition product **11**, 1-phenyl-2-propen-1-ol, exclusively in 51% yield with 54% ee (Table 7, entry 1). The absolute configuration of **11** proved to be *S* by comparison of the optical rotation with the literature value.[18] The choice of solvents is crucial for the enantioselectivity: 70% ee in toluene, 87% ee in dichloromethane (entries 2 and 3). Using Me-Pybox (**1b**) and *i*-Pr-Pybox (**1c**) derived acrolein complexes **10b**,**c**, the enantioselectivity decreased (entries 4 and 5). The reaction of **10a**,**b** with

(16) Recent 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 and imines: (d) Saito, S.; Kano, T.; Hatanaka, K.; Yamamoto, H. *J. Org. Chem.* **1997**, *62*, 5651. (e) Motoyama, Y.; Mikami, Y.; Kawakami, H.; Aoki, K.; Nishiyama, H. *Organometallics* **1999**, *18*, 3584. Asymmetric oxidation of sulfides: (f) Schenk, W. A.; Frosch, J.; Adam, W.; Prechtl, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1609.

(17) Organolithium reagents: (a) Mukaiyama, T.; Soai, K.; Sato, T.; Shimizu, H.; Suzuki, K. *J. Am. Chem. Soc.* **1979**, *101*, 1455. (b) Mazaleyrat, J.-P.; Cram, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 4585. (c) Eleveld, M. B.; Hogeveen, H. *Tetrahedron Lett.* **1984**, *25*, 5187. (d) Kanoh, S.; Muramoto, H.; Maeda, K.; Kawaguchi, N.; Motoi, M.; Suda, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2244. (e) Ye, M.; Lagaraj, S.; Jackman, L. M.; Hillegrass, K.; Hirsh, K. A.; Bollinger, A. M.; Grosz, A. L. *Tetrahedron* **1994**, *50*, 6109. (f) Huffman, M. A.; Yasuda, N.; DeCamp, A. E.; Grabowski, E. J. J. *J. Org. Chem.* **1995**, *60*, 1590. (g) Scharpwinkel, K.; Tull, S.; Schäfer, H. J. *Tetrahedron: Asymmetry* **1996**, *7*, 2497. (h) Thompson, A.; Corley, E. G.; Huntington, M. F.; Grabowski, E. J. J.; Remenar, J. F.; Collum, D. B. *J. Am. Chem. Soc.* **1998**, *120*, 2028. (i) Schön, M.; Naef, R. *Tetrahedron: Asymmetry* **1999**, *10*, 169. (j) Arvidsson, P. I.; Davidsson, Ö.; Hilmersson, G. *Tetrahedron: Asymmetry* **1999**, *10*, 527. Grignard reagents: (k) Tomioka, K.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1987**, *28*, 1291. (l) Weber, B.; Seebach, D. *Tetrahedron* **1994**, *50*, 6117. See also ref 15d.

(18) Kuffner, U.; Schlögl. K. *Monatsh. Chem.* **1972**, *103*, 1320.

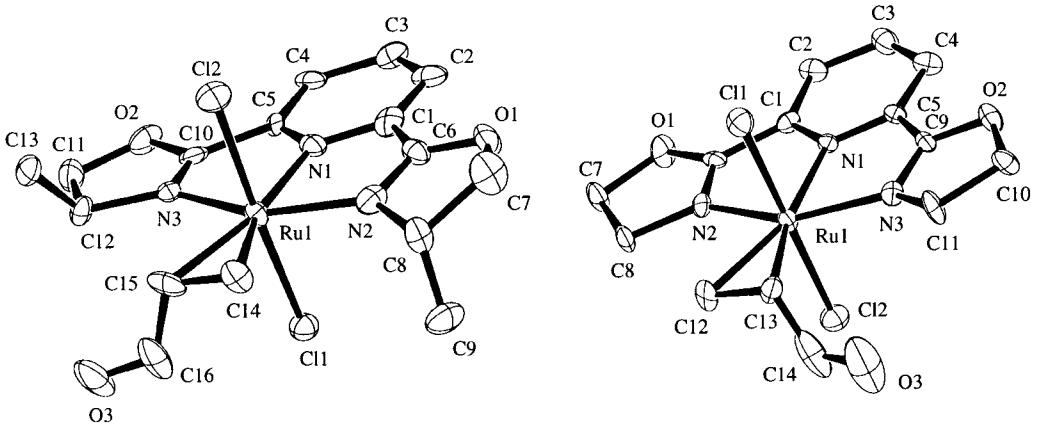


Figure 9. Molecular structures of (Me-Pybox)$RuCl_2$(η^2-acrolein) (**10b**) and (dH-Pybox)$RuCl_2$(η^2-acrolein) (**10d**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for (Me-Pybox)$RuCl_2$(η^2-acrolein) (10b)

Ru(1)−Cl(1)	2.401(4)	Ru(1)−Cl(2)	2.381(4)
Ru(1)−N(1)	2.02(2)	Ru(1)−N(2)	2.13(2)
Ru(1)−N(3)	2.16(2)	Ru(1)−C(14)	2.20(1)
Ru(1)−C(15)	2.24(2)	O(1)−C(6)	1.31(2)
O(1)−C(7)	1.53(2)	O(2)−C(10)	1.31(3)
O(2)−C(11)	1.42(2)	O(3)−C(16)	1.20(2)
N(1)−C(1)	1.36(2)	N(1)−C(5)	1.37(3)
N(2)−C(6)	1.32(2)	N(2)−C(8)	1.50(2)
N(3)−C(10)	1.25(2)	N(3)−C(12)	1.53(3)
C(14)−C(15)	1.42(4)		
Cl(1)−Ru(1)−Cl(2)	176.3(2)	Cl(1)−Ru(1)−N(1)	87.2(4)
Cl(1)−Ru(1)−N(2)	88.7(4)	Cl(1)−Ru(1)−N(3)	90.7(4)
Cl(1)−Ru(1)−C(14)	96.5(4)	Cl(1)−Ru(1)−C(15)	94.3(5)
Cl(2)−Ru(1)−N(1)	89.1(4)	Cl(2)−Ru(1)−N(2)	90.5(4)
Cl(2)−Ru(1)−N(3)	88.3(4)	Cl(2)−Ru(1)−C(14)	86.9(4)
Cl(2)−Ru(1)−C(15)	89.2(5)	N(1)−Ru(1)−N(2)	76.4(6)
N(1)−Ru(1)−N(3)	76.1(7)	N(1)−Ru(1)−C(14)	157(1)
N(1)−Ru(1)−C(15)	164.9(7)	N(2)−Ru(1)−N(3)	152.5(6)
N(2)−Ru(1)−C(14)	81(1)	N(2)−Ru(1)−C(15)	118.7(7)
N(3)−Ru(1)−C(14)	125(1)	N(3)−Ru(1)−C(15)	88.8(7)
C(14)−Ru(1)−C(15)	37(1)	C(6)−O(1)−C(7)	106(1)
C(10)−O(2)−C(11)	107(1)	C(6)−N(2)−C(8)	110(1)
C(10)−N(3)−C(12)	108(2)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for (dH-Pybox)$RuCl_2$(η^2-acrolein) (10d)

Ru(1)−Cl(1)	2.389(5)	Ru(1)−Cl(2)	2.397(5)
Ru(1)−N(1)	2.04(1)	Ru(1)−N(2)	2.11(1)
Ru(1)−N(3)	2.13(1)	Ru(1)−C(12)	2.20(1)
Ru(1)−C(13)	2.27(2)	O(1)−C(6)	1.31(2)
O(1)−C(7)	1.47(2)	O(2)−C(9)	1.36(2)
O(2)−C(10)	1.51(2)	O(3)−C(14)	1.33(2)
N(1)−C(1)	1.33(2)	N(1)−C(5)	1.34(2)
N(2)−C(6)	1.28(2)	N(2)−C(8)	1.50(2)
N(3)−C(9)	1.34(2)	N(3)−C(11)	1.49(2)
C(12)−C(13)	1.50(2)		
Cl(1)−Ru(1)−Cl(2)	179.2(2)	Cl(1)−Ru(1)−N(1)	90.2(3)
Cl(1)−Ru(1)−N(2)	91.0(4)	Cl(1)−Ru(1)−N(3)	86.7(4)
Cl(1)−Ru(1)−C(12)	87.7(5)	Cl(1)−Ru(1)−C(13)	83.2(7)
Cl(2)−Ru(1)−N(1)	89.1(3)	Cl(2)−Ru(1)−N(2)	88.5(4)
Cl(2)−Ru(1)−N(3)	93.4(4)	Cl(2)−Ru(1)−C(12)	92.8(5)
Cl(2)−Ru(1)−C(13)	97.5(7)	N(1)−Ru(1)−N(2)	75.8(4)
N(1)−Ru(1)−N(3)	77.2(5)	N(1)−Ru(1)−C(12)	158.2(5)
N(1)−Ru(1)−C(13)	161.3(6)	N(2)−Ru(1)−N(3)	152.8(5)
N(2)−Ru(1)−C(12)	82.6(5)	N(2)−Ru(1)−C(13)	121.6(6)
N(3)−Ru(1)−C(12)	124.3(5)	N(3)−Ru(1)−C(13)	85.0(6)
C(12)−Ru(1)−C(13)	39.3(6)	C(6)−O(1)−C(7)	107(1)
C(9)−O(2)−C(10)	108(1)	C(6)−N(2)−C(8)	107(1)
C(9)−N(3)−C(11)	111(1)		

PhMgBr in dichloromethane also gave the 1,2-addition product **11**, but the ee values were moderate (63−64%) (entries 6 and 7).

The observed absolute *S* configuration and enantioselectivity of the phenylated product **11** is explained by Figure 10. The acrolein is bound to the (*S,S*)-(Pybox)-$RuCl_2$ fragments by the *si* face of the C=C bond with an *s-trans* arrangement of the carbonyl moiety. Therefore, the *si* face of the C=O plane can be masked. The phenyllithium or phenylmagnesium reagents eventually attacked the exposed *re* face of the carbonyl group; therefore, the *S* product **11** was obtained.

Conclusions

Enantioface-selective olefin coordination of α,β-unsaturated carbonyl compounds to the chiral ruthenium bis(oxazolinyl)pyridine fragments has been demonstrated. The *si* enantioface of the C_α=C_β bonds can be perfectly differentiated, and the conformation of α,β-unsaturated carbonyl systems can be fixed into *s-trans* arrangements by binding to the (*S,S*)-(Pybox)$RuCl_2$ fragments. It was also clarified that this preferential π-face selection and *s-trans* conformation of α,β-unsaturated carbonyl compounds can be attributed to the C_2-symmetric and octahedral structure of the chiral (Pybox)-$RuCl_2$ system, which proved to act as efficient chiral assemblies for the asymmetric phenylation of acrolein with organometallic reagents, even in a stoichiometric manner. These findings may serve as a mechanistic view of new polymerization reactions recently developed.[19]

Experimental Section

General Methods. Anhydrous dichloromethane, tetrahydrofuran and phenyllithium were purchased from Kanto Chemical Co. Pyridine 2,6-dicarboxylic acid was purchased from Aldrich Chemical Co. Trimethyl orthoformate was purchased from Kishida Chemical Co. Xylene was distilled from sodium benzophenone ketyl immediately prior to use. ^{1}H and ^{13}C NMR spectra were measured on a JEOL GNM-270 (270 MHz) spectrometer. Chemical shifts for ^{1}H NMR were described in parts per million downfield from tetramethylsilane as an internal standard (δ 0) in $CDCl_3$, unless otherwise noted. Chemical shifts for ^{13}C NMR were expressed in parts per

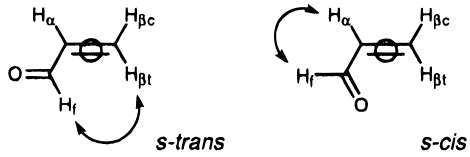
(19) Brookhart and Gibson found that the iron and cobalt complexes bearing N-N-N type tridentate ligands (N-N-N: 2,6-bis(imino)pyridine) act as olefin polymerization catalysts. See: (a) Small, B. L.; Brookhart, M.; Bennett, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (b) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143. (c) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849.

Table 5. Summary of the J_{C-H} Coupling Constants[a]

		δ (ppm)/J_{C-H} (Hz)		
entry	compd	C_α	C_β	C_f
1	acrolein (free)	137.1	137.6	193.5
		161.1	164.8	173.3
2	**10b**	78.5	78.6	**207.6**
		163.6	**155.0**	**184.3**
3	**10d**	79.8	75.5	**207.4**
		163.6	**156.3**	**188.9**

[a] In $CDCl_3$ (25 °C, TMS).

Table 6. Summary of NOE Data for Acrolein Complexes 10[a]



	NOE (saturated/observed, %)			
complex	H_f/H_α	$H_f/H_{\beta t}$	$H_{\beta t}/H_f$	H_α/H_f
10b		3	**13**	
10c	0	7	**12**	−5
10d	4	−1	**16**	2

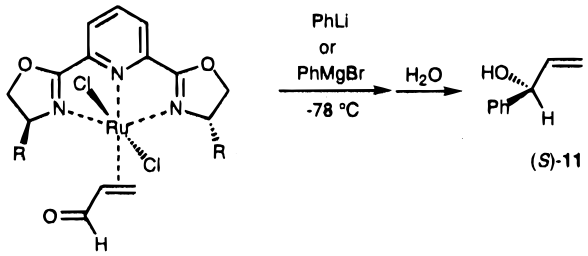
[a] In $CDCl_3$ (25 °C, TMS).

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 Yamato MP-21 and Yanaco MP-J3 instruments. Elemental analyses were measured on a Yanaco CHN CORDER MT-3. Optical rotations were measured on a JASCO DIP-140 polarimeter. Gas chromatography (GC) analyses were performed with a Shimadzu GC-14A gas chromatograph, and C-R5A chromatopac. 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 a 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 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. Pybox ligands, 2,6-bis(R-2-oxazolin-2-yl)pyridines (R = Ph, *i*-Pr, H), were prepared by our methods.[20] Ethylene complex **2a** was prepared by our method.[10b] $[(p\text{-cymene})RuCl_2]_2$ was prepared by the literature method.[21]

Synthesis of Me-Pybox (1b). Dimethyl 2,6-Pyridinedicarboxylate. To a stirred solution of pyridine 2,6-dicarboxylic acid (2.00 g, 12.0 mmol) and trimethyl orthoformate (2.9 mL, 26.3 mmol) in MeOH (20 mL) was added 3 drops of concentrated H_2SO_4 at room temperature. After it was stirred for 26 h at that temperature, the reaction mixture was quenched by the addition of saturated $NaHCO_3$ and evaporated under reduced pressure to remove MeOH. Then the residue was extracted with dichloromethane and dried over Na_2SO_4. Concentration of the organic layer gave dimethyl 2,6-pyridinedicarboxylate in 96% yield (2.25 g) as a white solid which was used in the next step without further purification. ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.03 (s, 6H), 8.03 (t, J = 7.8 Hz, 1H), 8.32 (d, J = 7.8 Hz, 2H).

(20) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics* **1991**, *10*, 500.
(21) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 223.

Table 7. Asymmetric Phenylation of Acrolein Complexes 10[a]



10a: R = Ph
10b: R = Me
10c: R = *i*-Pr

entry	complex	Ph-M	solvent	% yield	% ee[b]
1	**10a**	PhLi	THF	51	54
2	**10a**	PhLi	toluene	75	70
3	**10a**	PhLi	CH_2Cl_2	89	87
4	**10b**	PhLi	CH_2Cl_2	70	43
5	**10c**	PhLi	CH_2Cl_2	71	81
6	**10a**	PhMgBr	CH_2Cl_2	61	63
7	**10b**	PhMgBr	CH_2Cl_2	61	64

[a] All reactions were carried out using 0.1 mmol of acrolein complexes **10** and 0.2 mmol of PhLi (in ether) or PhMgBr (in ether) in 2 mL of solvent at −78 °C. [b] Determined by capillary GC analysis using Astec GT-A-30M, or chiral HPLC analysis using Daicel CHIRALCEL OD.

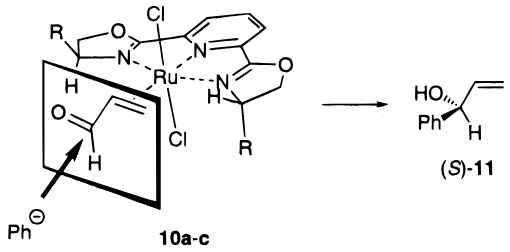


Figure 10.

2,6-Bis[(2′-(*S*)-hydroxymethyl)ethylcarbamoyl]pyridine. To a stirred solution of dimethyl 2,6-pyridinedicarboxylate (5.40 g, 27.7 mmol) in xylene (200 mL) was added (*S*)-alaninol (5.00 g, 66.6 mmol), and the reaction mixture was heated at 100 °C under a nitrogen atmosphere. After the mixture was heated for 72 h, white precipitates was filtered and washed with a small amount of xylene to give 2,6-bis[(2′-(*S*)-hydroxymethyl)ethylcarbamoyl]pyridine in 96% yield (7.51 g, 26.7 mmol), which was used in the next step without further purification. IR (KBr): 3312, 2996, 1643, 1537, 1441, 1246, 1036, 738 cm^{-1}. ^{1}H NMR (270 MHz, THF-d_6): δ 1.38 (d, J = 7.0 Hz, 6H), 2.70 (bs, 2H), 3.70 (s, 4H), 4.25 (m, 2H), 8.16 (t, J = 7.8 Hz, 1H), 8.39 (d, J = 7.8 Hz, 2H).

2,6-Bis[(2′-(*S*)-chloromethyl)ethylcarbamoyl]pyridine. A solution of $SOCl_2$ (11.7 mL, 160 mmol) in chloroform (20 mL) was added dropwise to a solution of 2,6-bis[(2′-(*S*)-hydroxymethyl)ethylcarbamoyl]pyridine obtained as above (7.51 g, 26.7 mmol) in tetrahydrofuran (40 mL) and chloroform (300 mL) at 0 °C under a nitrogen atmosphere. After it was refluxed for 4 h, the reaction mixture was poured into water (100 mL) and neutralized with $NaHCO_3$. Then the water phase was extracted with dichloromethane and dried over $MgSO_4$. Concentration of the organic layer gave 2,6-bis[(2′-(*S*)-chloromethyl)ethylcarbamoyl]pyridine in 97% yield (8.27 g, 26.0 mmol), which was used in the next step without further purification. IR (KBr): 2976, 1649, 1527, 1443, 1365, 1208, 738 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.42 (d, J = 7.0 Hz, 6H), 3.77 (dd, J = 11.2, 3.2 Hz, 2H), 3.86 (d, J = 11.2, 3.8 Hz, 2H), 4.59 (dddq, J = 7.3, 3.8, 3.2, 7.0 Hz, 2H), 7.99 (d, J = 7.3 Hz, 2H), 8.05 (t, J = 7.8 Hz, 1H), 8.34 (d, J = 7.8 Hz, 2H).

2,6-Bis[4′-(*S*)-methyloxazolin-2′-yl]pyridine (Me-Pybox; 1b). To a suspension of NaH (2.64 g, 66.0 mmol) in THF (300 mL) was added 2,6-bis[(2′-(*S*)-chloromethyl)ethylcarbamoyl]pyridine (7.00 g, 22.0 mmol). After it was stirred at 35 °C for 1 h, the reaction mixture was poured into water at 0 °C and evaporated under reduced pressure. Then the residue was extracted with dichloromethane and dried over Na_2SO_4. Concentration of the organic layer gave 2,6-bis[4′-(*S*)-methyloxazolin-2′-yl]pyridine (Me-Pybox; **1b**) in 98% yield (5.26 g, 21.5 mmol). $[\alpha]^{20}_D = -129.4°$ (*c* 1.0, CH_2Cl_2). Mp: 169 °C. IR (KBr): 2968, 1632, 1366, 1261, 1113, 1062, 740 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 1.38 (d, J = 7.0 Hz, 6H), 4.07 (dd, J = 8.1, 8.0 Hz, 2H), 4.43 (ddq, J = 9.7, 8.0, 7.0 Hz, 2H), 4.62 (dd, J = 9.7, 8.1 Hz, 2H), 7.86 (t, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.4, 62.4, 74.8, 125.6, 137.3, 147.0, 162.3. Anal. Found for $C_{13}H_{15}N_3O_2$: C, 63.76; H, 6.05; N, 17.03. Calcd: C, 63.66; H, 6.16; N, 17.13.

General Procedure for the Synthesis of Olefin Complexes. (Ph-Pybox)RuCl$_2$(η^2-dimethyl fumarate) (3a). To a stirred solution of [(*p*-cymene)$RuCl_2$]$_2$ (61 mg, 0.1 mmol) and dimethyl fumarate (29 mg, 0.2 mmol) in dichloromethane (2.0 mL) was added Ph-Pybox (74 mg, 0.2 mmol) under a nitrogen atmosphere. After it was stirred for 1 h at 25 °C, the reaction mixture was concentrated under reduced pressure. Then the residue was washed with ether in hexane to remove dissociated *p*-cymene, giving crude *trans*-(Ph-Pybox)$RuCl_2$(η^2-methyl fumarate) (**3a**), and this crude product was measured by NMR. ^1H NMR (270 MHz, $CDCl_3$): δ 3.28 (s, 6H), 4.73 (t, J = 8.8 Hz, 2H), 5.34 (dd, J = 10.7, 8.8 Hz, 2H), 5.64 (s, 2H), 6.48 (dd, J = 10.7, 8.8 Hz, 2H), 7.19−7.46 (m, 10H), 7.99−8.16 (m, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 49.7, 68.8, 69.4, 79.4, 124.4, 128.2, 128.4, 128.6, 137.8, 138.3, 146.3, 164.7, 174.9.

(Me-Pybox)RuCl$_2$(η^2-dimethyl fumarate) (3b). ^1H NMR (270 MHz, $CDCl_3$): δ 1.39 (d, J = 6.8 Hz, 6H), 3.68 (s, 6H), 4.68 (dd, J = 8.8, 3.9 Hz, 2H), 4.84 (ddq, J = 8.3, 3.9, 6.8 Hz, 2H), 5.06 (dd, J = 8.8, 8.3 Hz, 2H), 6.21 (s, 2H), 7.96−8.12 (m, 3H).

(*i*-Pr-Pybox)RuCl$_2$(η^2-dimethyl fumarate) (3c). ^1H NMR (270 MHz, $CDCl_3$): δ 0.73 (d, J = 6.4 Hz, 6H), 1.02 (d, J = 7.3 Hz, 6H), 2.15 (m, 2H), 3.66 (s, 6H), 4.79−4.97 (m, 4H), 5.45 (m, 2H), 6.18 (s, 2H), 7.91 (d, J = 7.3 Hz, 2H), 8.06 (t, J = 7.3 Hz, 1H).

(Ph-Pybox)RuCl$_2$(η^2-dimethyl maleate) (4a). ^1H NMR (270 MHz, $CDCl_3$): δ 3.36 (s, 3H), 3.47 (s, 3H), 4.03 (d, J = 10.8 Hz, 1H), 4.90 (d, J = 10.8 Hz, 1H), 5.00 (t, J = 8.8 Hz, 1H), 5.15−5.37 (m, 3H), 5.58−5.71 (m, 2H), 7.29−7.40 (m, 6H), 7.52−7.60 (m, 4H), 7.70−7.82 (m, 3H).

(*i*-Pr-Pybox)RuCl$_2$(η^2-dimethyl maleate) (4c). ^1H NMR (270 MHz, $CDCl_3$): δ 0.93 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 7.8 Hz, 6H), 1.00 (d, J = 6.8 Hz, 3H), 2.76−2.94 (m, 2H), 3.42 (s, 3H), 3.48 (s, 3H), 4.62 (m, 1H), 4.70−4.97 (m, 5H), 5.21 (d, J = 11.5 Hz, 1H), 5.30 (d, J = 11.5 Hz, 1H), 7.57−7.73 (m, 3H).

(Ph-Pybox)RuCl$_2$(η^2-maleic anhydride) (5a). The product was purified by silica gel chromatography (100:1 dichloromethane/methanol) at 0 °C in 85% yield. Mp: 224 °C dec. IR (KBr): 3079, 1833, 1754, 1498, 1407, 1242, 907, 697 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 4.84 (dd, J = 8.4, 4.6 Hz, 2H), 5.30 (dd, J = 9.7, 8.4 Hz, 2H), 5.78 (d, J = 4.9 Hz, 1H), 5.89 (d, J = 4.9 Hz, 1H), 5.98 (dd, J = 9.7, 4.6 Hz, 2H), 7.20−7.44 (m, 10H), 8.16−8.35 (m, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 68.9, 71.2, 72.0, 81.0, 125.4, 127.0, 128.9, 138.0, 138.2, 145.4, 165.2, 171.2, 174.0. Anal. Found for $C_{27}H_{21}N_3O_5Cl_2Ru\cdot 0.5MeOH$: C, 50.45; H, 3.64; N, 6.66. Calcd: C, 50.39; H, 3.54; N, 6.41.

(Me-Pybox)RuCl$_2$(η^2-maleic anhydride) (5b). The product was purified by silica gel chromatography (10:1 dichloromethane/acetone) at 0 °C in 63% yield. Mp: 117 °C dec. IR (KBr): 3061, 2969, 1830, 1753, 1578, 1496, 1407, 1246, 1066, 910, 755 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 1.52 (d, J = 6.3 Hz, 6H), 4.74−4.82 (m, 2H), 4.97−5.15 (m, 4H), 6.05 (d, J = 5.2 Hz, 1H), 6.48 (d, J = 5.2 Hz, 1H), 8.07 (d, J = 6.8 Hz, 2H), 8.19 (t, J = 6.8 Hz, 6H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.4, 62.6, 70.4, 79.6, 124.7, 138.5, 145.5, 163.8, 173.9. Anal. Found for $C_{17}H_{17}N_3O_5Cl_2Ru\cdot 0.5$(acetone): C, 40.82; H, 3.63; N, 7.71. Calcd: C, 40.82; H, 3.70; N, 7.72.

(Ph-Pybox)RuCl$_2$(η^2-cinnamaldehyde) (6a). ^1H NMR (270 MHz, $CDCl_3$): δ 4.53−4.68 (m, 2H), 5.20−5.36 (m, 4H), 6.41 (dd, J = 15.6, 8.3 Hz, 1H), 6.91 (d, J = 15.6 Hz, 1H), 7.08−7.79 (m, 18H), 9.31 (d, J = 8.3 Hz, 1H).

(Ph-Pybox)RuCl$_2$(σ-cynnamonitrile) (7a). The product was purified by alumina chromatography (200:1 dichloromethane/methanol) at 0 °C in 99% yield. Mp: 224 °C dec. IR (KBr): 3464, 2224, 1479, 1425, 1387, 966, 696 cm^{-1}. ^1H NMR (270 MHz): δ 4.56 (dd, J = 11.6, 7.6 Hz, 2H), 5.45 (d, J = 16.5 Hz, 1H), 6.50 (d, J = 16.5 Hz, 1H), 7.18−7.82 (m, 18H). ^{13}C NMR (67.8 MHz): δ 69.5, 78.2, 95.9, 123.0, 127.0, 128.0, 128.1, 128.3, 128.8, 128.9, 129.3, 130.8, 133.6, 137.7, 150.1, 151.5, 167.4. Anal. Found for $C_{32}H_{26}N_4O_2Cl_2Ru$: C, 57.37; H, 4.01; N, 8.24. Calcd: C, 57.32; H, 3.91; N, 8.36.

(*i*-Pr-Pybox)RuCl$_2$(σ-cynnamonitrile) (7c). The product was purified by alumina chromatography (500:1 dichloromethane/methanol) at 0 °C in 92% yield. Mp: 212 °C dec. IR (KBr): 3452, 2924, 2220, 1461, 1391, 960, 753 cm^{-1}. ^1H NMR (270 MHz): δ 1.01 (d, J = 10.7 Hz, 6H), 1.04 (d, J = 10.7 Hz, 6H), 2.50−2.68 (m, 2H), 4.33 (dd, J = 7.3, 3.4 Hz, 1H), 4.37 (dd, J = 7.3, 3.4 Hz, 1H), 4.75 (dd, J = 8.8 Hz, 2H), 4.86 (dd, J = 10.3, 8.8 Hz, 2H), 6.47 (d, J = 16.6 Hz, 1H), 7.50 (d, J = 16.6 Hz, 1H), 7.40−7.70 (m, 8H). ^{13}C NMR (67.8 MHz): δ 16.0, 19.4, 29.9, 70.2, 71.8, 96.6, 122.5, 127.3, 128.9, 129.1, 129.5, 131.2, 133.6, 150.6, 151.1, 165.4. Anal. Found for $C_{26}H_{30}N_4O_2Cl_2Ru$: C, 51.71; H, 5.08; N, 9.25. Calcd: C, 51.83; H, 5.02; N, 9.30.

(Ph−Pybox)RuCl$_2$(η^2-methyl acrylate) (8a). The product was purified by silica gel chromatography (100:1 dichloromethane/methanol) at −60 °C in 86% yield. Single crystals for the X-ray diffraction study were obtained from dichloromethane/ether at room temperature. Mp: 167 °C dec. IR (KBr): 3461, 3062, 1702, 1585, 1488, 1398, 1255, 970, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 3.45 (s, 3H), 4.73 (dd, J = 8.6, 8.4 Hz, 2H), 4.90 (dd, J = 8.5, 1.6 Hz, 1H), 5.12 (dd, J = 12.2, 8.5 Hz, 1H), 5.25 (dd, J = 12.2, 1.6 Hz, 1H), 5.30 (dd, J = 10.6, 8.6 Hz, 2H), 6.04 (m, 2H), 7.27−7.45 (m, 10H), 8.05 (s, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 49.9, 68.8, 69.9, 74.3, 79.3, 124.2, 127.8, 128.3, 128.4, 135.4, 138.7, 146.1, 164.8, 175.2. Anal. Found for $C_{27}H_{25}N_3O_4Cl_2Ru\cdot 0.5CH_2Cl_2$: C, 49.38; H, 3.95; N, 6.38. Calcd: C, 49.30; H, 3.91; N, 6.27.

(Me-Pybox)RuCl$_2$(η^2-methyl acrylate) (8b). The product was purified by silica gel chromatography (100:1 dichloromethane/methanol) at −60 °C in 83% yield. Mp: 107 °C dec. IR (KBr): 1698, 1487, 1397, 1066, 949, 817, 751 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 1.48 (d, J = 6.2 Hz, 6H), 3.70 (s, 3H), 4.67 (dd, J = 8.3, 3.9 Hz, 2H), 5.00 (dd, J = 8.8, 8.3 Hz, 2H), 5.09 (ddq, J = 8.8, 3.9, 6.2 Hz, 2H), 5.30 (dd, J = 8.8, 2.0 Hz, 1H), 5.76 (dd, J = 12.2, 8.8 Hz, 1H), 5.87 (dd, J = 12.2, 2.0 Hz, 1H), 7.90−8.00 (m, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.7, 51.7, 61.4, 69.8, 72.0, 78.5, 123.8, 135.6, 146.3, 163.5, 175.4. Anal. Found for $C_{17}H_{21}N_3O_4Cl_2Ru\cdot {}^2/_3CH_2Cl_2$: C, 37.86; H, 3.98; N, 7.59. Calcd: C, 37.89; H, 4.02; N, 7.50.

(*i*-Pr-Pybox)RuCl$_2$(η^2-methyl acrylate) (8c). ^1H NMR (270 MHz, $CDCl_3$): δ 0.74 (d, J = 6.4 Hz, 6H), 1.03 (d, J = 7.3 Hz, 6H), 2.26−2.46 (m, 2H), 3.71 (s, 3H), 4.72−4.98 (m, 6H), 5.29 (dd, J = 8.3, 2.0 Hz, 1H), 5.78 (dd, J = 11.7, 8.3 Hz, 1H), 5.87 (dd, J = 11.7, 2.0 Hz, 1H), 7.86−8.04 (m, 3H).

(Ph−Pybox)RuCl$_2$(η^2-methyl vinyl ketone) (9a). The product was purified by silica gel chromatography (100:1 dichloromethane/methanol) at −60 °C in 95% yield. Mp: 115 °C dec. IR (KBr): 3457, 3072, 1660, 1486, 1400, 1245, 970, 698 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 1.63 (s, 3H), 4.76 (dd, J = 8.6, 7.3 Hz, 2H), 5.06 (d, J = 9.7 Hz, 1H), 5.07 (d, J = 12.2 Hz, 1H), 5.23 (dd, J = 12.2, 9.7 Hz, 1H), 5.30 (dd, J = 10.3, 8.6 Hz, 2H), 5.95 (dd, J = 10.3, 7.3 Hz, 2H), 7.20−7.46 (m, 10H), 8.06 (s, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 29.4,

Table 8. Crystallographic Data for 8a and 10b,d

	8a	10b	10d
formula	$C_{27}H_{25}N_3O_4Cl_2Ru$	$C_{16}H_{19}N_3O_3Cl_2Ru$	$C_{14}H_{17}N_3O_4Cl_2Ru$
fw	627.49	473.32	463.28
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1$	$P2_1/c$
cell constants			
a, Å	10.545(2)	7.149(1)	10.369(1)
b, Å	22.999(4)	10.669(2)	10.942(2)
c, Å	10.770(1)	11.928(1)	15.402(2)
β, deg	92.76(1)	98.10(1)	103.424(9)
V, Å^3	2608.9(8)	900.7(2)	1699.6(5)
Z	4	2	4
D_{calcd}, g cm^{-3}	1.597	1.745	1.810
$F(000)$	1272	476	928
μ(Mo Kα), cm^{-1}	8.45	11.87	12.60
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	50.0	54.9	49.9
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan rate, deg min^{-1}	8.0 (in ω), up to 3 scans	16.0 (in ω), up to 5 scans	4.0 (in ω), up to 3 scans
no. of total data collected	4945	2350	2648
no. of unique data	4680 (R_{int} = 0.039)	2184 (R_{int} = 0.059)	2468 (R_{int} = 0.043)
no. of obsd rflns	2374 ($I > 3\sigma$)	1245 ($I > 3\sigma$)	1320 ($I > 3\sigma$)
no. of variables	334	225	217
residuals: R; R_w	0.054; 0.045	0.047; 0.042	0.058; 0.044

68.3, 75.0, 78.1, 79.6, 124.3, 128.1, 128.5, 128.6, 135.5, 138.8, 146.4, 165.0, 212.4. Anal. Found for $C_{27}H_{25}N_3O_3Cl_2Ru$: C, 52.97; H, 4.07; N, 6.93. Calcd: C, 52.91; H, 4.02; N, 6.99.

(Me-Pybox)RuCl$_2$(η^2-methyl vinyl ketone) (9b). The compound was purified by silica gel chromatography (5:1 dichloromethane/acetone) at −60 °C in 92% yield. Mp: 142 °C dec. IR (KBr): 2979, 1653, 1487, 1397, 1256, 1094, 963, 816, 749 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.50 (d, J = 6.5 Hz, 6H), 2.27 (s, 3H), 4.65−4.76 (m, 2H), 4.87−5.05 (m, 4H), 5.44 (dd, J = 8.3, 1.5 Hz, 1H), 5.71−5.86 (m, 2H), 7.91−8.05 (m, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.7, 29.5, 60.5, 72.7, 78.4, 79.3, 123.7, 137.4, 146.3, 163.5, 211.7. Anal. Found for $C_{17}H_{21}N_3O_3Cl_2Ru\cdot{}^1/_3CH_2Cl_2$: C, 40.36; H, 4.23; N, 8.16. Calcd: C, 40.37; H, 4.23; N, 8.15.

(*i*-Pr-Pybox)RuCl$_2$(η^2-methyl vinyl ketone) (9c). ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.99 (d, J = 6.8 Hz, 6H), 1.08 (d, J = 7.3 Hz, 6H), 2.29 (s, 3H), 2.32−2.46 (m, 2H), 4.68−4.96 (m, 6H), 5.44 (dd, J = 8.3, 1.0 Hz, 1H), 5.79 (dd, J = 12.7, 1.0 Hz, 1H), 5.88 (dd, J = 12.7, 8.3 Hz, 1H), 7.91−8.04 (m, 3H).

(Ph-Pybox)RuCl$_2$(η^2-acrolein) (10a). The product was purified by silica gel chromatography (10:1 dichloromethane/acetone) at −60 °C in 93% yield. Mp: 86 °C dec. IR (KBr): 3459, 2923, 1675, 1459, 1398, 1257, 970, 696 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.78 (dd, J = 8.4, 7.3 Hz, 2H), 4.90−5.20 (m, 3H), 5.29 (dd, J = 9.3, 8.4 Hz, 2H), 5.74 (dd, J = 9.3, 7.3 Hz, 2H), 7.20−7.55 (m, 10H), 8.09 (s, 3H), 9.32 (d, J = 7.8 Hz, 1H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 77.3, 77.6, 79.6, 124.5, 127.9, 128.6, 128.7, 135.7, 138.4, 145.8, 164.9, 207.9. Anal. Found for $C_{26}H_{23}N_3O_3Cl_2Ru$: C, 52.36; H, 3.86; N, 6.88. Calcd: C, 52.27; H, 3.88; N, 7.03.

(Me-Pybox)RuCl$_2$(η^2-acrolein) (10b). The product was purified by silica gel chromatography (5:1 dichloromethane/acetone) at −60 °C in 96% yield. Single crystals for the X-ray diffraction study were obtained from dichloromethane/ethyl acetate at room temperature. Mp: 151 °C dec. IR (KBr): 3436, 1667, 1489, 1393, 1260, 1140, 1093, 965, 743 cm^{-1}. ^{1}H NMR (270 MHz): δ 1.54 (d, J = 6.5 Hz, 6H), 4.69 (dd, J = 8.3, 3.9 Hz, 2H), 4.83 (ddq, J = 8.8, 3.9, 6.5 Hz, 2H), 4.99 (dd, J = 8.8, 8.3 Hz, 2H), 5.06 (dd, J = 8.4, 1.9 Hz, 1H), 5.64 (ddd, J = 10.8, 8.4, 7.3 Hz, 1H), 6.02 (dd, J = 10.8, 1.9 Hz, 1H), 7.90−8.10 (m, 3H), 9.76 (d, J = 7.3 Hz, 1H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 21.8, 60.9, 75.0, 78.5, 78.6, 124.0, 136.0, 146.1, 163.7, 207.6. Anal. Found for $C_{20}H_{27}N_3O_3Cl_2Ru$: C, 40.59; H, 4.07; N, 8.77. Calcd: C, 40.60; H, 4.05; N, 8.88.

(*i*-Pr−Pybox)RuCl$_2$(η^2-acrolein) (10c). The product was purified by silica gel chromatography (100:1 dichloromethane/methanol) at −60 °C in 91% yield. Mp: 248 °C dec. IR (KBr): 3477, 2964, 1673, 1488, 1398, 966 cm^{-1}. ^{1}H NMR (270 MHz): δ 0.78 (d, J = 6.8, 6H), 1.08 (d, J = 7.3 Hz, 6H), 2.46 (m, 2H), 4.65 (m, 2H), 4.82 (dd, J = 9.2, 8.4 Hz, 2H), 4.93 (dd, J = 8.4, 3.5 Hz, 2H), 5.58 (dd, J = 8.1, 1.6 Hz, 1H), 5.67 (ddd, J = 11.3, 8.1, 7.8 Hz, 1H), 6.05 (dd, J = 11.3, 1.6 Hz, 1H), 7.90−8.10 (m, 3H), 9.78 (d, J = 7.8 Hz, 1H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 14.3, 18.9, 29.6, 71.9, 75.0, 78.5, 123.8, 135.8, 145.6, 163.4, 207.4. Anal. Found for $C_{20}H_{27}N_3O_3Cl_2Ru\cdot 0.5MeOH$: C, 45.20; H, 5.36; N, 7.39. Calcd: C, 45.14; H, 5.36; N, 7.70.

(dH-Pybox)RuCl$_2$(η^2-acrolein) (10d). The product was purified by silica gel chromatography at −60 °C in 96% yield. Single crystals for the X-ray diffraction study were obtained from dichloromethane/ethyl acetate at room temperature. Mp: 265 °C dec. IR (KBr): 3458, 1679, 1495, 1397, 1275, 959 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.07−4.40 (m, 2H), 4.40−4.66 (m, 2H), 5.07 (t, J = 9.3 Hz, 4H), 5.39 (m, 1H), 5.59 (d, J = 7.8 Hz, 1H), 5.71 (d, J = 11.2 Hz, 1H), 7.82−8.15 (m, 10H), 9.75 (d, J = 7.8 Hz, 1H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 52.2, 71.9, 75.5, 79.8, 123.7, 136.1, 145.6, 164.6, 207.4. Anal. Found for $C_{14}H_{15}N_3O_3Cl_2Ru$: C, 37.80; H, 3.89. Calcd: C, 37.76; H, 3.40.

General Procedure for the Alkylation Reaction of Acrolein Complexes with Phenyllithium. 1-Phenyl-2-propene-1-ol (11). To a stirred solution of (Me-Pybox)RuCl$_2$(η^2-acrolein) (**10b**; 94.6 mg, 0.2 mmol) in dichloromethane (3 mL) was added a 2 N solution of phenyllithium in ether/cyclohexane (426 mL, 0.4 mmol) for 1 min at −78 °C under an argon atmosphere. After it was stirred for 10 min at that temperature, the reaction mixture was poured into water in hexane, then filtered through a pad of Celite and Florisil. Purification by silica gel chromatography (5:1 hexane/ether) gave 1-phenyl-2-propene-1-ol (**11**; 18.9 mg, 0.14 mmol) in 70% yield. $[\alpha]^{25}_D$ = −2.8° (*c* 0.78, benzene; 43% ee, *S*); lit.[18] $[\alpha]_D$ = −5.8° (*c* 5.0, benzene). IR (neat): 3366, 3063, 2869, 1641, 1493, 1451, 1195, 1024, 990, 835, 760 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.96 (d, J = 1.1 Hz, 1H), 5.20 (dd, J = 6.5, 1.1 Hz, 1H), 5.21 (dd, J = 10.3, 0.8 Hz, 1H), 5.36 (dd, J = 17.0, 0.8 Hz, 1H), 6.06 (ddd, J = 17.0, 10.3, 6.5 Hz, 1H), 7.22−7.42 (m, 5H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 75.3, 115.0, 126.3, 127.7, 128.5, 140.3, 142.7.

The % ee was determined by chiral capillary GC (Astec G-TA-30M, column temperature 120 °C, detection FID; t_R = 16.5 min (*R*), 17.4 min (*S*)) or chiral HPLC analysis (Daicel

CHIRALCEL OD, UV detector 230 nm, 9:1 hexane/*i*-PrOH, flow rate 0.5 mL/min; $t_R = 15.0$ min (*S*), 16.6 min (*R*)).

X-ray Structure Determination and Details of Refinement. X-ray-quality crystals of **8a** and **10b**,**d** 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 Kα radiation; $\lambda = 0.710\ 69$ Å. The lattice parameters and orientation matrices were obtained and refined from 25 machine-centered reflections with $27.41 < 2\theta < 29.58°$ for **8a**, with $28.81 < 2\theta < 29.87°$ for **10b**, and with $24.32 < 2\theta < 28.33°$ for **10d**. 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 8.

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 2374 observed reflections ($I > 3\sigma(I)$) and 334 variable parameters for **8a**, on 1245 observed reflections ($I > 3\sigma(I)$) and 225 variable parameters for **10b**, and on 1320 observed reflections ($I > 3\sigma(I)$) and 217 variable parameters for **10d**. 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 8, and the numbering schemes employed are shown in Figures 7 and 9, which were drawn with ORTEP at the 30% probability ellipsoid level.

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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 of **8a** and **10b**,**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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