Planar Chiral (η^6-Arene) Ruthenium Cp Complexes in Organic Synthesis: Diastereoselective Complexation of Arene Compounds with Benzylic Alcohol and Its Synthetic Application to Chiral Biaryls

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1-*o*-Substituted phenylethanols gave diastereoselective ruthenium Cp complexes via coordination of ruthenium with benzylic oxygen. This reaction can be further applied to the diastereoselective ruthenium complexation of δ-lactone-bridged biaryls possessing a chiral benzyl alcohol function at the side chain. Although δ-lactone-bridged biphenyls **10a** and **10b** exist as an inseparable equilibrated atropisomeric mixture, the corresponding ruthenium complexes **11a** and **11b** were obtained as a single compound, respectively, with differentiated arene face complexation and fixation of the central bond. Analogous biaryl compound **15** with a naphthalene fragment gave three Cp ruthenium complexes, **16**, **17**, and **18**, in various ratios depending on reaction temperature. Naphthalene ring-coordinated ruthenium complex **16** was isomerized to the complex **17** via axial isomerization and ruthenium fragment migration to the inverted arene face by heating at 50 °C in dichloroethane, and the ruthenium complexes **16** and **17** were further transformed to benzene ring-coordinated ruthenium complex **18** by heating at 90 °C. The diastereoselective ruthenium complexation with fixation (and isomerization) of the axial bond of δ-lactone-bridged biaryls **10** and **15** was supported by ab initio calculations. Also, the ab initio calculations of δ-lactone-bridged biaryl ruthenium complexes with a naphthalene fragment were well consistent with the experimental results. The obtained ruthenium complexes of δ-lactone-bridged biaryls afforded axially chiral biaryls by ring opening of δ-lactone with nonchiral reagents.

Introduction

(η^6-Arene)transition metal complexes are well recognized as versatile intermediates in organic synthesis as a consequence of their electron-withdrawing ability and steric bulkiness of the transition metal. Particularly, η^6-arene chromium complexes have been most extensively studied in organic reactions.[1] In contrast to the arene chromium complexes, isoelectronic (η^6-arene)ruthenium Cp^+ complexes have received comparatively little attention despite the mild conditions for their preparation and air stability.[2] Representative studies are inter- or intramolecular nucleophilic substitution of (η^6-halobenzene)Ru^+Cp complexes and base-induced benzylic alkylation due to the strong electron-withdrawing ability of the RuCp fragment. Pearson et al. reported the synthesis of a biaryl ether fragment of vancomycin-related antibiotics by using a cationic arene ruthenium complex.[2i,j] This method is particularly useful for the formation of the large-membered biaryl ether part of vancomycin antibiotics, since the corresponding tricarbonylchromium complexes are inaccessible. Furthermore, η^6-arene ruthenium complexes exist in two enantiomeric forms based on planar chirality when the arene ring is substituted with different substituents at the 1,2- or 1,3-position. This feature leads to a useful procedure

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(1) (a) Semmelhack, M. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier Science, Ltd.: Oxford, 1995; Vol. 12, pp 979−1015, 1017−1038. (b) Davies, S. G.; McCarthy, T. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier Science, Ltd.: Oxford, 1995; Vol. 12, pp 1039−1070. (c) Schmalz, H.-G.; Siegel, S. In *Transition Metals for Fine Chemicals and Organic Synthesis*; Bolm, C., Beller, M., Eds.; VCH: Weinheim, 1998; Vol. 1. (d) Kaliappan, K. P.; Kündig, E. P. *Chem. Rev.* **2000**, *100*, 2917−2940. (e) Rose-Munch, F.; Rose, E. *Eur. J. Inorg. Chem.* **2002**, 1269−1283. (f) Rose-Munch, F.; Rose, E. *Curr. Org. Chem.* **1999**, *3*, 445−467.

(2) Representative examples: (a) Pigge, F. C.; Coniglio, J. J. *Curr. Org. Chem.* **2001**, *5*, 757−784. (b) Pigge, F. C.; Fang, S.; Rath, N. P. *Org. Lett.* **1999**, *1*, 1851−1854. (c) Pigge, F. C.; Fang, S.; Rath, N. P. *Tetrahedron Lett.* **1999**, *40*, 2251−2254. (d) Pearson, A. J.; Chelliah, M. V. *J. Org. Chem.* **1998**, *63*, 3087−3098. (e) Janetka, J. W.; Rich, D. H. *J. Am. Chem. Soc.* **1997**, *119*, 6488−6495. (f) Komatsuzaki, N.; Uno, M.; Kikuchi, H.; Takahashi, S. *Chem. Lett.* **1996**, 677−678. (g) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485−488. (h) Moriarty, R. M.; Gill, U. S.; Ku, Y. Y. *J. Organomet. Chem.* **1988**, *350*, 157−190. (i) Pearson, A. J.; Bignan, G. *Tetrahedron Lett.* **1996**, *37*, 735−738. (j) Pearson, A. J.; Gelormini, A. M. *J. Org. Chem.* **1994**, *59*, 4561−4570.

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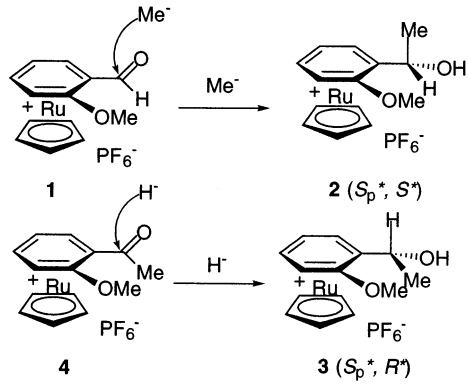
for asymmetric reaction together with one face block by the ruthenium fragment. However, although the synthesis of planar chiral Ru complexes with an unsymmetrically substituted *cyclopentadienyl* ligand has been studied,[3] only few efforts have been reported for the preparation of enantiomerically pure (η^6-arene)ruthenium complexes with different substituents on the *arene ring*.[4,5] To the best of our knowledge, only one example of the synthesis of an enantiomerically pure (η^6-arene)-ruthenium Cp complex is achieved by transformation of central chirality to planar chirality of the resulting π-arene ruthenium complex. Thus, a planar chiral ruthenium complex can be prepared by aromatization of the Cp*Ru complex obtained from dihydrocarvone and $[Cp^*RuOMe]_2$ by dehydrogenative complexation.[5] However, this strategy has a limitation with respect to the variety of enantiomerically pure starting materials. A straightforward strategy to obtain enantiomerically pure or enriched planar chiral π-arene ruthenium complexes is therefore demanded for the development of asymmetric reactions. As part of our program on asymmetric syntheses utilizing the planar chiral arene transition metal complexes, we herein report on the stereoselective synthesis of planar chiral (arene)ruthenium Cp^+ complexes of *ortho*-substituted phenylethanol and related compounds and their synthetic application to axially chiral biaryls.

Results and Discussion

Stereoselective Nucleophilic Addition to Ruthenium Cp Complexes of *o*-Substituted Acetophenone and Benzaldehydes. Stereoselective transformations of the side chain utilizing the planar chirality of (η^6-arene)chromium complexes are well established.[1,6] Applying these methodologies, both diastereomers of 1-(*ortho*-substituted phenyl)ethyl alcohol ruthenium Cp complex can be prepared with high selectivity (Table 1). Thus, addition of MeLi or MeMgBr to the *o*-methoxy benzaldehyde ruthenium Cp complex (**1**) proceeds with high diastereoselectivity to give (*S**,*S**)-diastereomer **2** (entries 1 and 2). On the other hand, (*o*-methoxyacetophenone)ruthenium complex (**4**) afforded predominantly diastereomeric (*S**,*R**)-complex **3** by reduction (entries 3 and 4). The diastereoselectivity of these reactions is based on the *exo*-addition of nucleophiles to the carbonyl group of the ruthenium complexes **1** and **4**, in which the carbonyl oxygen is placed far from the *o*-methoxy group because of stereoelectronic repulsion. However, the synthesis of enantiomerically enriched starting materials is problematic, although high diastereoselectivity can be achieved in the nucleophilic addition reactions.

Table 1. Diastereoselective Nucleophilic Addition to the *ortho*-Substituted (Arene)ruthenium Cp Complexes



entry	complex	nucleophile	ratio (**2**:**3**)	yield (%)
1	**1**	MeMgBr	>99:1	94
2	**1**	MeLi	92:8	42
3	**4**	$NaBH_4$	33:67	98
4	**4**	$LiAlH_4$	30:70	73

Diastereoselective Ru Cp Complexation of 1-*o*-Substituted Phenylethanol. A rigorous approach to prepare optically pure planar chiral arene π-complexes would be diastereoselective complexation of arenes bearing a chiral substituent. Extremely high diastereoselectivity in the π-complexation to distinguish the arene face was observed in cases where the chiral center is part of an annelated ring close to the arene. For example, enantiopure 1-tetralol and related compounds gave predominantly (1-*endo* tetralol)chromium complex via coordination with a benzylic hydroxy group by ligand transfer of naphthalene $Cr(CO)_3$.[7] This complexation would be further expected to take place with high selectivity even in acyclic compounds. In line with this consideration, we examined diastereoselective ruthenium complexation of arenes possessing a chiral benzylic alcohol function.[8] 1-*o*-Methoxyphenylethanol (**5a**) was refluxed with $[CpRu(CH_3CN)_3]PF_6$[9] in dichloroethane to give (S_p*,*S**)-Ru complex **6a** in 93% yield with 92/8 dr (Table 2, entry 1). With more bulky methyl- or trimethylsilyl-substituted phenylethanols, the diastereoselectivities of $CpRu^+$ complexation increased slightly (entries 2 and 3). The relative configuration of **6a** was determined by X-ray crystallography after acetylation.[10] On the other hand, in the $CpRu^+$ complexation of 1-*o*-methylphenyl ethyl acetate (**5d**), the diastereoselectivity was considerably decreased (entry

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(4) Thermal replacement of the acetonitrile ligand from the planar chiral substituted Cp-Ru$(MeCN)_3$ system to prochiral arenes gave planar chiral arene ruthenium Cp-complexes with moderate selectivity: Komatsuzaki, N.; Kikuchi, H.; Yamamoto, M.; Uno, M.; Takahashi, S. *Chem. Lett.* **1998**, 445−446.

(5) Pasch, R.; Koelle, U.; Ganter, B.; Englert, U. *Organometallics* **1997**, *16*, 3950−3958.

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(7) A representative reference. Schmalz, H.-G.; Millies, B.; Bats, J. W.; Dürner, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 631.

(8) Kamikawa, K.; Furusyo, M.; Uno, T.; Sato, Y.; Konoo, A.; Bringmann, G.; Uemura, M. *Org. Lett.* **2001**, *3*, 3667−3670.

(9) Trost, B. M.; Older, C. M. *Organometallics* **2002**, *21*, 2544−2546.

(10) Crystal structure data of acetylation of **6a**: Experimental formula = $C_{16}H_{19}O_3RuPF_6$, fw = 505.36, orthorhombic, space group $P2_12_12_1$ (#19), a = 14.600(3) Å, b = 17.926(2) Å, c = 7.136(2) Å, V = 1867.7(5) Å^3, Z = 4, $Dcacl$ = 1.797 g cm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-165780. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

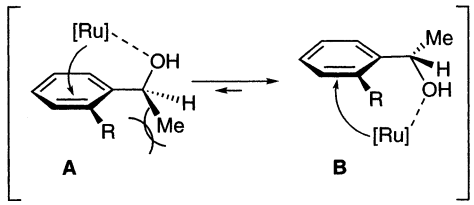
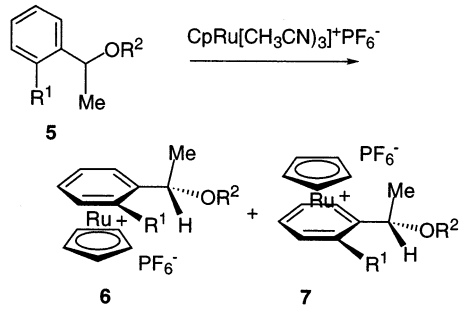


Figure 1. Proposed transition state.

Table 2. Diastereoselective Ruthenium Complexation Reaction of 2-Substituted Secondary Benzyl Alcohols 5



entry	compound	R^1	R^2	ratio (**6**:**7**)	yield (%)
1	**5a**	OMe	H	92:8	93
2	**5b**	Me	H	94:6	84
3	**5c**	Me_3Si	H	95:5	86
4	**5d**	Me	Ac	71:29	85

4). Obviously, this ruthenium complexation takes place with high diastereoselectivity via coordination of the ruthenium with the benzylic oxygen atom even in an acyclic series. Of the two proposed transition states **A** and **B**, the conformation **B** is favorable for giving (S_p*,*S**)-Ru complex **6** due to minimum nonbonded interaction between the *ortho* substituent and the methyl groups (Figure 1).

Synthesis of Planar Chiral Ruthenium Complexes of Biaryl Lactones: Axially Chiral Biaryl Synthesis. One of us already reported that biaryls connected with a *δ*-lactone bridge gave the corresponding chromium or ruthenium complexation products.[11] These transition metal-coordinated biaryls were usually obtained as axially equilibrated compounds without distinction of the arene face in *racemic* form. Furthermore, most *δ*-lactone-bridged biaryls without the transition metal coordination to the arene ring are configurationally unstable at the biaryl axis.[11] However, these nonchiral, axially equilibrated compounds are useful intermediates for asymmetric synthesis of axially chiral biaryls. Thus, the *δ*-lactone rings of axially equilibrated biaryls were opened with *chiral O*-nucleophiles via dynamic kinetic resolution to give optically active biaryls.[12] However, the variety of chiral nucleophiles used in this *δ*-lactone ring opening is limited for the preparation of axially chiral biaryls. Therefore, we have extended this arene face differential ruthenium complexation to *δ*-lactone-linked biaryl compounds possessing a chiral benzyl alcohol function at the side chain for further development of *δ*-lactone-bridged biaryls in asymmetric synthesis.

Synthesis of Enantiomerically Pure *δ*-Lactone-Bridged Biaryls. Enantiomerically pure *δ*-lactone-bridged biaryls possessing a secondary benzyl alcohol function as the starting materials in this study were prepared as follows (Scheme 1). CBS-reduction[13] of acetophenone derivatives **8a** and **8b** with (*S*)-oxazaborolidine and BH_3·Me_2S gave (*R*)-alcohols **9a** and **9b** with high enantiomeric excess in a quantitative yield. Subsequent intramolecular palladium-catalyzed coupling with a combination of $Pd(OAc)_2$ and 2-di-*tert*-butylphosphinobiphenyl[14] produced the desired diastereomeric biaryl *δ*-lactones **10a** and **10a′** as an inseparable 2:1 atropisomeric mixture in 69% yield. The atropisomerization barrier of these two diastereomers was measured by dynamic ^{1}H NMR studies of coalescence of two independent signals at 110 °C. The activation free energy was calculated as 17.01 kcal mol^{-1} based on the Eyring equation.[15] Theoretical calculations[16] showed that the diastereomer **10a** was 1.12 kcal mol^{-1} more stable than **10a′** in total energy, and the atropisomerization barrier was estimated as 17.77 kcal mol^{-1} (Table 3), in good agreement with the experimental value. Thus, these two axial diastereomers can be observed at room temperature. A sterically less substituted biaryl lactone, the methoxy analogue **10b**, was also prepared by the same reaction sequence. The palladium-catalyzed coupling of optically active alcohol **9b** produced the desired biaryl as a single diastereomer in 60% yield without detection of any stereoisomers. Rapid interconversion between **10b** and **10b′** is considered feasible by decreasing the steric demand.[17]

Diastereoselective Ruthenium Complexation of Biaryl Lactones. With the optically active *δ*-lactone-bridged biaryl in hand, we next studied the Ru(II)$^+$Cp complexation of the diastereomeric mixture of **10a** and **10a′**. Surprisingly, a ruthenium complex **11a** was obtained as a single axially chiral diastereomer in 51% yield[18] without formation of any stereo- and regioisomers by treatment with $[CpRu(CH_3CN)_3]PF_6$ under the same conditions.[19] The formation as a single diastere-

(11) (a) Bringmann, G.; Heubes, M.; Breuning, M.; Göbel, L.; Ochse, M.; Schöner, B.; Schupp, O. *J. Org. Chem.* **2000**, *65*, 722−728. (b) Bringmann, G.; Wuzik, A.; Stowasser, R.; Rummey, C.; Göbel, L.; Stalke, D.; Pfeiffer, M.; Schenk, W. A. *Organometallics* **1999**, *18*, 5017−5021. (c) Bringmann, G.; Göbel, L. *Inorg. Chim. Acta* **1994**, *222*, 255−260.

(12) The corresponding homologous seven-membered lactone biaryls are stable towards axial equilibration. (a) Bringmann, G.; Hinrichs, J.; Henschel, P.; Peters, K.; Peters, E.-M. *Synlett* **2000**, 1822−1824. (b) Bringmann, G.; Hartung, T.; Kröcher, O.; Gulden, K.-P.; Lange, J.; Burzlaff, H. *Tetrahedron* **1994**, *50*, 2831−2840. (c) Bringmann, G.; Breuning, M.; Tasler, S. *Synthesis* **1999**, *4*, 525−558.

(13) (a) Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1986−2012. (b) Xavier, L. C.; Mohan, J. J.; Mathre, D. J.; Thompson, A. S.; Carroll, J. D.; Corley, E. G.; Desmond, R. *Org. Synth.* **1991**, *74*, 50−71.

(14) (a) Aranyous, A.; Old, D. W.; Kiyomori, A.; Wolf, J. P.; Sadighi, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4369−4378. (b) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2413−2416.

(15) Ernst, L. *Chem. Unserer Zeit* **1983**, *17*, 21−31.

(16) Geometry optimizations were carried out with B3LYP hybrid density functional theory on using 6-31G* (C, H, O) and LACVP (Ru) basis sets with the Gaussian 98 and Jaguar V3.5 suite of programs.

(17) Theoretical calculations (B3LYP/6-31*) showed that the atropoisomerization barrier between axial diastereomers **10b** and **10b′** is estimated at 8.68 kcal mol^{-1}.

(18) The described values are purified yields of crude products (~70%) after a recrystallization for removal of the contaminant ruthenium reagent along with 10% yield of the starting materials. The diastereoselectivity of the ruthenium complexation was determined for the crude products by NMR spectra, and the stereo- and regioisomers were not observed by ^{1}H NMR spectra of the crude products of **11a** and **11b**.

(19) The corresponding $Cr(CO)_3$ complex was not formed by treatment of **10** with $Cr(CO)_6$ or (naphthalene)$Cr(CO)_3$.

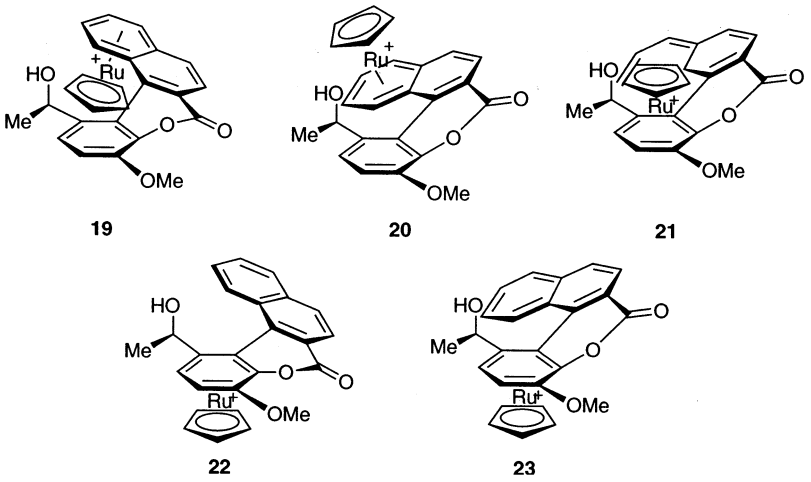
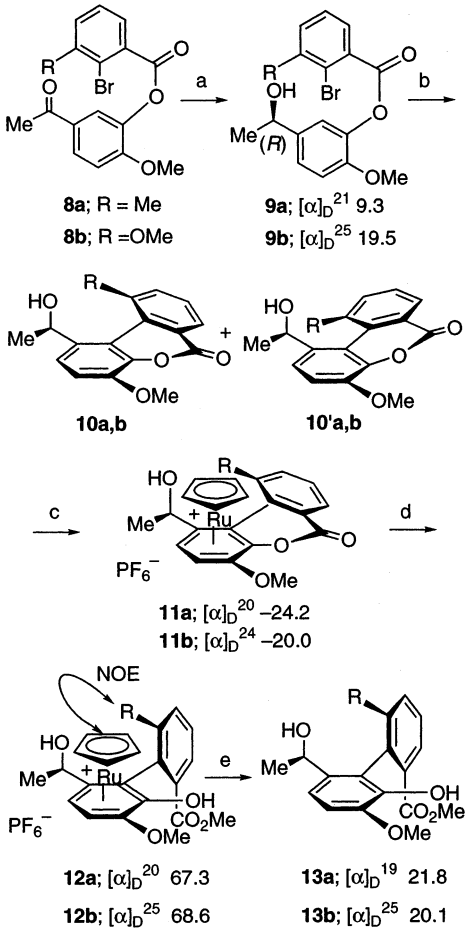


Figure 2. Structures of **19**−**23**.

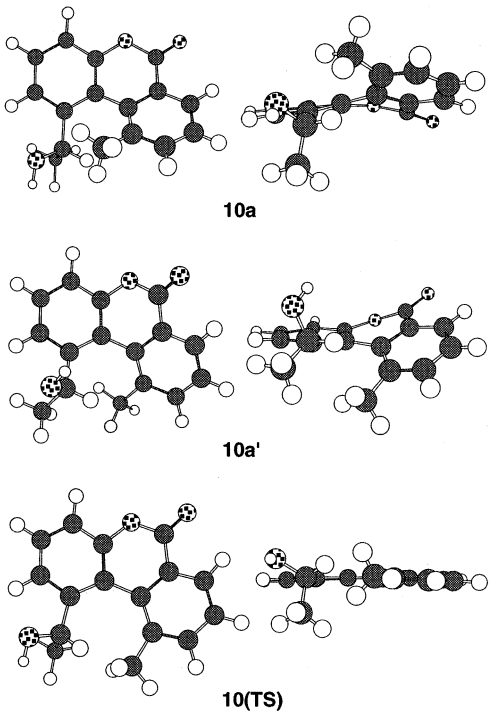
Scheme 1[a]



[a] Reaction conditions: (a) BH_3·Me_2S, (*S*)-oxazaborolidine (20 mol %), THF, rt (99%, 97% ee from **8a**; 99%, 98% ee from **8b**); (b) $Pd(OAc)_2$, (10 mol %), 2-(di-*tert*-butylphosphino)biphenyl (20 mol %), NaOAc, DMA, 100 °C (69% from **9a**; 60% from **9b**); (c) $[CpRu(CH_3CN)_3]PF_6$, $(CH_2Cl)_2$, reflux (51% from **10a** and **10a′**; 48% from **10b** or **10b′**); (d) NaOMe, MeOH (98% from **11a**; 99% from **11b**); (e) *hν*, CH_3CN (95% from **12a**; 98% from **12b**).

omer is in sharp contrast to the previous report[11b,c] that the related δ-lactone-linked biaryl compound without stereogenic center gave an inseparable mixture of chromium complexes. The configuration of **11a** was determined by X-ray analysis.[20] The Cp ruthenium fragment was coordinated to the arene ring substituted

Table 3. Total Energy E_{total} and Relative Energy E_{rel} of the Biaryl Lactone at the B3LYP/6-31G* Level



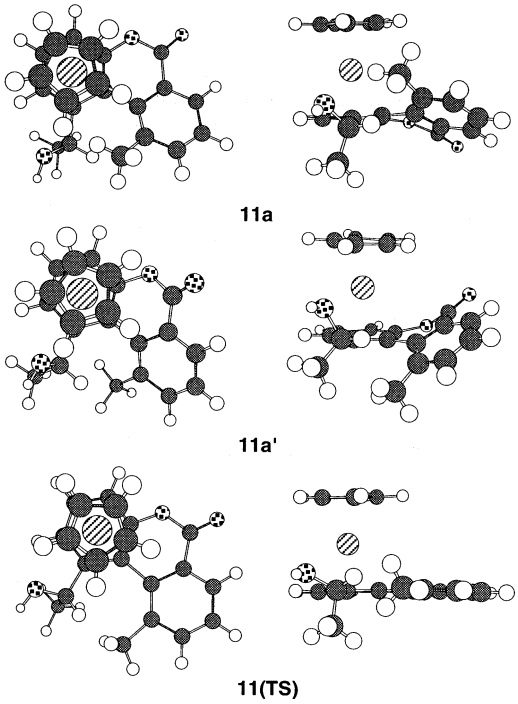
entry	compound	E_{total} (Hartrees)	E_{rel} (kcal/mol)[a]
1	**10a**	−843.81005	0.00
2	**10a′**	−843.80850	1.12[a]
3	**10a(TS)**	−843.78257	17.77[b]

[a] Including zero-point correction. [b] Including free-energy correction at 298.15 K.

with the electron-donating hydroxymethyl and methoxy groups via an interaction of the ruthenium with the benzylic oxygen. The axial chirality of the complex **11a** was found to be the *S*-configuration. The complex **11a** is by 2.1 kcal mol^{-1} more stable than the corresponding

(20) Crystal structure data of **11a**. Experimental formula = $C_{22}H_{21}O_4PF_6Ru$, fw = 595.44, orthorhombic, space group *Pbcn* (#60), *a* = 16.953(3) Å, *b* = 15.441(2) Å, *c* = 20.454(2) Å, *V* = 5354(2) $Å^3$, *Z* = 8, *Dcacl* = 1.477 gcm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-165781.

Table 4. Total Energy E_{total} and Relative Energy E_{rel} of the Ruthenium Complex at the B3LYP/ (6-31G*/LACVP) Level



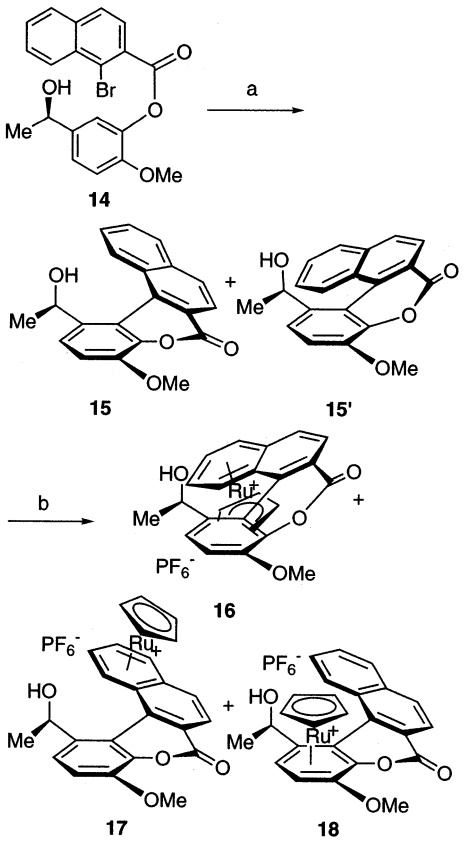
entry	complex	E_{total} (Hartrees)	E_{rel} (kcal/mol)
1	**11a**	−1131.03916	0.00
2	**11a′**	−1131.03520	2.10[a]
3	**11(TS)**	−1131.01742	14.12[b]

[a] Including zero-point correction. [b] Including free-energy correction at 298.15 K.

R-configured diastereomer **11a′** by ab initio calculations (Table 4).[16] This value is larger than the difference (1.12 kcal mol^{-1}) of the total energies between the pre-ruthenium complexation diastereomers **10a** and **10a′**. Although the precise mechanism for the formation of ruthenium complex **11a** as a single axial diastereomer is not clear, the complex **11a** might be formed as a thermodynamically stable compound via axial isomerization of the diastereomeric *R*-axial ruthenium complex derived from the diastereomer **10a′** under the reaction conditions. An alternative mechanism may be considered: the ruthenium complexation takes place from a distinct face of only diastereomer **10a** via dynamic kinetic resolution of the axially equilibrated diastereomers **10a** and **10a′**. Similarly, the ruthenium complexation of methoxy analogues **10b** and **10b′** gave a single axially chiral ruthenium complex **11b** without the formation of any stereo- and regioisomers in 48% yield. In this way, the equilibrated axially diastereomeric biaryls linked with the δ-lactone ring gave a thermodynamically stable atropisomeric compound as a single isomer by ruthenium complexation to the distinguished arene face.[21]

With the enantiopure axially chiral ruthenium-complexed δ-lactone biaryls in hand, we next focused on the ring opening of the δ-lactones **11a** and **11b** with

Scheme 2[a]



[a] Reaction conditions: (a) $Pd(OAc)_2$, (10 mol%), 2-(di-*tert*-butylphosphino)biphenyl (20 mol%), NaOAc, DMA, 100 °C (67%); (b) $[CpRu(CH_3CN)_3]PF_6$, $(CH_2Cl)_2$.

nonchiral reagents. The ruthenium complexes **11a** and **11b** were treated with NaOMe in methanol at room temperature to give a single diastereomer[22] of axially chiral *ortho*-tetrasubstituted biaryl ruthenium complexes **12a** and **12b** in 98% and 99% yields, respectively. The relative configuration was elucidated by differential NOE experiments and an opposite face attack of a nucleophile to the transition metal fragment. Thus, 7% NOE was observed between the methyl group on the ruthenium-free arene ring and the Cp ring of **12a**. Finally, demetalation of the complexes **12a** and **12b** gave axially chiral biaryls **13a** and **13b** in good yields. Furthermore, stereoselective reduction of the lactone ring of **11b** with $LiAlH_4$ gave the corresponding axially chiral biaryl as a single diastereomer in 99% yield.[23]

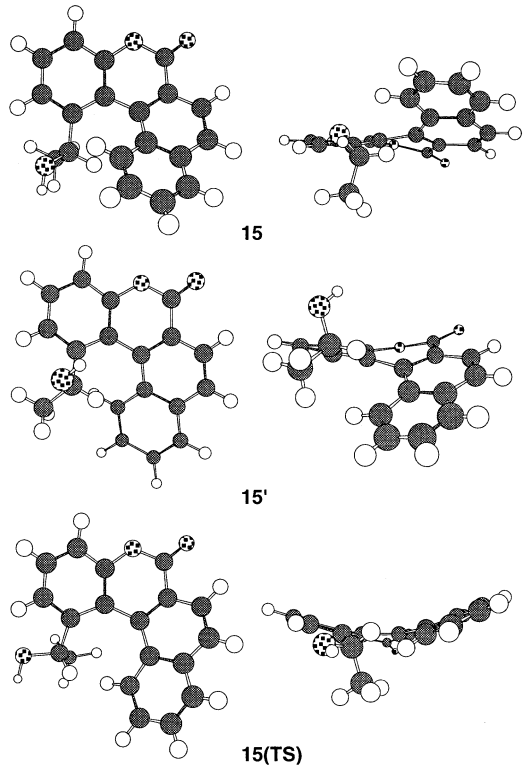
Ruthenium Complexation of Biaryl δ-Lactone with Naphthyl Fragment. As a further extension of the differential face ruthenium complexation, we next examined the biaryl δ-lactone with a naphthyl fragment (Scheme 2). Palladium-catalyzed coupling produced the desired diastereomeric biaryl δ-lactones **15** and **15′** as an inseparable 2:1 atropisomeric mixture. The atropisomerization barrier of these two diastereomers was calculated as 22.74 kcal mol^{-1}, and the diastereomer **15** was 1.51 kcal mol^{-1} more stable than **15′** in total energy (Table 5). In this case, stereo- and regioisomeric ruthe-

(21) A naphthyltetrahydroisoquinoline skeleton with a chiral center having sterically bulky substituents and specific nitrogen substitution could also fix the axial axis of δ-lactone-bridged biaryls by palladium-catalyzed cyclization: see ref 12c.

(22) The δ-lactone ring opening of the ruthenium-uncomplexed biaryls **10** with NaOMe gave a diastereomeric mixture of axially atropisomeric biaryls (dr = 7:3 for **10a**; 1:1 for **10b**) based on the axially equilibrated ratio of **10a** and **10b**.

(23) Interestingly, a related ruthenium-complex biaryl lactone ring could be opened only with *O*-nucleophiles: see ref 10b.

Table 5. Total Energy E_{total} and Relative Energy E_{rel} of the Biaryl Lactone at the B3LYP/6-31G* Level



entry	compound	E_{total} (Hartrees)	E_{rel} (kcal/mol)
1	**15**	−985.13853	0.00
2	**15′**	−958.13611	1.51[a]
3	**15(TS)**	−958.10235	23.45[b]

[a] Including zero-point correction. [b] Including free-energy correction at 298.15 K.

Table 6. Ruthenium Complexation Reaction of Biaryl Lactones 15 and 15′

entry	temp (°C)	ratio (**16**:**17**:**18**)	yield (%)
1	25	52:48:0	54
2	50	10:90:0	56
3	90	0:0:100	60

nium complexes were obtained in various ratios dependent on the reaction conditions (Table 6). Thus, when a diastereomeric mixture (2:1) of **15** and **15′** was conducted with $[CpRu(CH_3CN)_3]PF_6$ in dichloroethane at 25 °C, ruthenium complexes **16** and **17** coordinated on the distal part of the naphthalene ring were obtained as a 1:1 mixture (entry 1). The ruthenium complex **17** was predominantly obtained by performance at 50 °C (entry 2). Interestingly, when the complexation reaction took place at 90 °C, the benzene ring-coordinated Cp ruthenium complex **18** was obtained as a sole product without formation of the ruthenium complexes **16** and **17** (entry 3). Furthermore, the complex **16** was isomerized to the diastereomeric ruthenium complex **17** by heating in dichloroethane at 50 °C. In addition, both ruthenium complexes **16** and **17** were converted to the benzene ring-coordinated ruthenium complex **18** by heating at 90 °C. The stereochemistry of the obtained ruthenium Cp complexes was determined by X-ray crystallography.[24]

For understanding of the regio- and stereoselectivity of the ruthenium complexation on the naphthyl compounds **15** and **15′** depending on the reaction conditions, ab initio calculations of the total energy in possible diastereomers have been studied, and the results are summarized in Table 7. Thermodynamical stability of these eight possible ruthenium complexes was found to follow the order **18** > **21** > **17** > **22** > **23** > **16** > **19** > **20**. These ab initio calculation data agree with the experimental result that the benzene ring-coordinated ruthenium Cp complex **18** was the thermodynamically most stable diastereomer. Among the four naphthalene ring-coordinated ruthenium complexes, the ruthenium complex **17** with *S*-axial configuration is the most stable.

Table 7. Total Energy E_{total} and Relative Energy E_{rel} of the Ruthenium Lactones

entry	compound	E_{total} (Hartrees)	E_{rel}[a] (kcal/mol)
1	**18**	−1245.42653	0.00
2	**21**	−1245.42116	2.94
3	**17**	−1245.42088	3.38
4	**22**	−1245.42078	3.55
5	**23**	−1245.42012	3.69
6	**16**	−1245.41718	5.51
7	**19**	−1245.41760	5.64
8	**20**	−1245.41303	8.55

[a] B3LYP/(6-31++G**/LACVP++**) level one-point energy calculation using B3LYP/(6-31G*/LACVP*) level optimized structure (including zero-point correction).

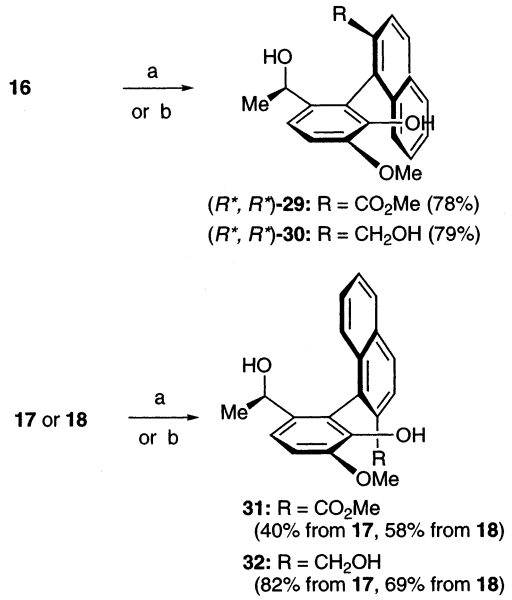
The formation and transformation of Cp ruthenium complexes **16**, **17**, and **18** would be explained as follows (Scheme 3). The naphthalene ring-coordinated ruthenium complex **17** might be formed by the Cp ruthenium migration to the inverted arene face of **19** after axial isomerization of the ruthenium complex **16** with *R*-axial configuration. This unique ruthenium migration path to the inverted arene face was recently found in a sterically demanding η^6-arene chromium complex possessing a heteroatom at the benzylic position in our group.[25] The migration of the transition metal to the inverted arene face takes place via coordination with the heteroatom for releasing steric repulsion between the metal fragment and the substituents. Furthermore, the naphthalene ring-coordinated ruthenium complex **17** transformed to the benzene ring-coordinated ruthenium complex **18** through same face slippage of the ruthenium.

An alternative reaction path for the formation of the complex **17** is axial isomerization of the thermodynami-

(24) Stereochemistry of **16** was determined by X-ray crystallography of ring-opening product **16′**. Experimental formula = $C_{26}H_{25}O_4PF_6Ru$, fw = 663.50, orthorhombic, space group *Fdd*2 (#43), a = 37.636(3) Å, b = 9.8968(7) Å, c = 28.323(2) Å, V = 10549.6(1) Å^3, Z = 16, *Dcacl* = 1.671 g cm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-188409. Crystal structure data of **17′** (PF_6^- of **17** was exchanged for BPh_4^- to improve crystallinity). Experimental formula = $C_{49}H_{41}BO_4Ru$, fw = 805.74, monoclinic, space group $P2_1/n$ (#14), a = 10.611(2) Å, b = 24.729(4) Å, c = 15.120(4) Å, b = 104.846(5)°, V = 3834.8(1) Å^3, Z = 4, *Dcacl* = 1.395 g cm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-188410. Crystal structure data of **18** after changing the counteranion from PF_6^- to BPh_4^-. Experimental formula = $C_{49}H_{41}O_4BRu$, fw = 805.74, monoclinic, space group $P2_1/n$ (#14), a = 12.8110(8) Å, b = 15.7839(9) Å, c = 18.829(1) Å, β = 95.880(3)°, V = 3787.4(3) Å^3, Z = 4, *Dcacl* = 1.413 g cm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-188411.

(25) Watanabe, T.; Shakadou, M.; Uemura, M. *Synlett* **2000**, 1141−1144. Details of stereoselective tricarbonylchromium migration to the inverted arene face will be published.

Scheme 3[a]



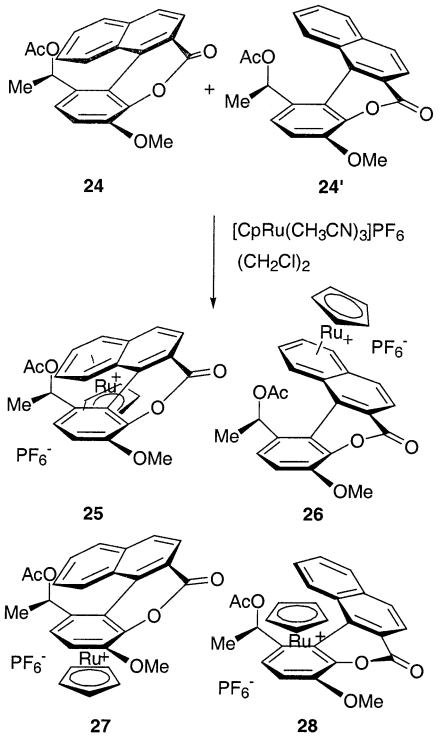
[a] Reaction conditions: (a) (1) NaOMe, (2) hν/CH_3CN; (b) (1) $NaBH_4$, (2) hν/CH_3CN.

cally unstable complex **20**, which would be formed by differential arene face ruthenium complexation of **15′**. The coordination of the benzyl alcohol function with ruthenium metal seems to play an important role for axial isomeization and face inversion of the $CpRu^+$ fragment as well as face differential complexation. Therefore, the ruthenium complexation and thermal behavior was next studied on a 2:1 mixture of the corresponding diastereomeric acetoxy derivatives **24** and **24′**. The results of ruthenium complexation are summarized in Table 8.

The naphthalene ring-coordinated ruthenium complexes **25** and **26** were obtained as a diastereomeric mixture in nearly the same ratio by heating at 50 °C. When the ruthenium complexation was carried out at 90 °C, two benzene ring-coordinated complexes, **27** and **28**, were obtained. The stereochemistry of the acetoxy ruthenium complexes **25**, **26**, and **28** was verified by comparison with authentic acetoxy complexes derived from free-hydroxy complexes **16**, **17**, and **18**, respectively, and the structure of **27** was determined by X-ray crystallography.[26] Furthermore, only a small amount (5−10%) of the distal naphthalene ring-coordinated ruthenium complex **25** was changed to the isomerized ruthenium complex **26** under heating in dichloroethane for 5 h, while the free-hydroxylated ruthenium complex **16** was easily isomerized to the complex **17** under the same conditions as mentioned above. Interestingly, the corresponding free-hydroxylated ruthenium complex **23** was not obtained by the complexation of free-hydroxy δ-lactone-linked naphthalene derivatives **15** and **15′** as shown in Table 6. The benzene ring-coordinated ruthenium complexes **27** and **28** would be formed through

(26) Crystal structure data of **27** after changing the counteranion from PF_6^- to BPh_4^-. Experimental formula = $C_{51}H_{43}O_5BRu$, fw = 847.73, monoclinic, space group $P2_1/c$ (#14), a = 17.1016(6) Å, b = 9.5927(3) Å, c = 25.6074(1) Å, β = 105.1970(1)°, V = 4054.0(3) Å^3, Z = 4, $Dcacl$ = 1.389 g cm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-191528.

Table 8. Ruthenium Complexation Reaction of Biaryl Lactones 24 and 24′



entry	temp (°C)	ratio (**25**:**26**:**27**:**28**)	yield (%)
1	25	67:33:0:0	70
2	50	50:50:0:0	72
3	90	18:35:27:20	63

same face slippage of the ruthenium fragment from the naphthalene ring-coordinated ruthenium complexes **25** and **26**, respectively. Furthermore, the rate of slippage was slower than the benzyl alcohol ruthenium complexes **16** and **17**. The acetoxy ruthenium complexes **25** and **26** produced only 15% yield of the benzene ring-coordinated ruthenium complexes along with recovery of the starting materials in 60% yield under heating at 90 °C in dichloroethane. Thus, the benzylic hydroxy group is essential not only for the axial isomerization and the migration of the $CpRu^+$ fragment to the inverted arene faces but also for the slippage of the Cp ruthenium fragment from naphthalene to the benzene ring. Although the precise mechanism of these isomerization reactions is still unclear at the present time, labilization of a metal−arene π-bond caused by the coordination of the heteroatom is essential for these reactions. Finally, we focused on the ring opening of δ-lactones **16**, **17**, and **18** with *nonchiral* reagents (Scheme 3). The ruthenium complex **16** was treated with NaOMe in methanol at room temperature and following demetalation of the complex gave *ortho*-tetrasubstituted biaryl **29** as a single diastereomer in 78% yield. On the other hand, the ruthenium complexes **17** and **18** gave atropisomeric diastereomer **31**. The relative configuration was elucidated by X-ray crystallography. Furthermore, stereoselective reduction of the lactone ring of **16**, **17**, and **18** with $NaBH_4$ gave the corresponding axially chiral biaryl as a single diastereomer **30** or **32** possessing the same axial chirality mentioned above in good yields.

In conclusion, we have developed a diastereoselective ruthenium complexation of 2-substituted secondary benzyl alcohol and the related δ-lactone-bridged biaryls to the distinct arene face and asymmetric synthesis of enantiomerically pure axially chiral biaryls.

Experimental Section

All manipulations involving organometallics were carried out under an atmosphere of nitrogen or argon and using an inert gas/vacuum double manifold technique. All melting points were determined on a Yanagimoto MPJ-2 micromelting point apparatus and were uncorrected. ^{1}H NMR spectra were measured on a JEOL ECP-500, EX-270 instrument, and all NMR spectra were recorded in $CDCl_3$ or acetone-d_6 solvent with tetramethylsilane as internal reference. IR spectra were determined on a JASCO A-100 spectrometer. Elemental analyses were performed on a Perkin-Elmer Model 240C and a Perkin-Elmer Model 2400 automatic analyzer. Mass spectra were determined on a JEOL JMS-DX303 with EI mode. Optical rotations were obtained on a JASCO DIP-370 automatic polarimeter at wavelength 589 nm (sodium D line) using a 1.0 dm cell with a total volume of 5 mL. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl immediately before use.

Diastereoselective Addition Reaction to Ruthenium Complexes: Preparation of Complex 2 by MeMgBr Addition. To a solution of *o*-methoxybenzaldehyde ruthenium complex **1** (150 mg, 0.34 mmol) in a mixture of dry THF (30.0 mL) and dichloromethane (3.0 mL) was added MeMgBr (0.77 mL, 0.67 mmol, 0.87 M in THF) at −20 °C under argon. The resulting solution was stirred for 3 h at −20 °C and quenched with water (2.0 mL). The reaction mixture was filtered off, and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel chromatography with CH_2Cl_2/acetone to give the ruthenium complex **2** (148 mg, 94%) as colorless crystals: mp 135 °C; ^{1}H NMR (270 MHz, acetone-d_6) δ 1.45 (3H, d, J = 6.6 Hz, CH_3), 3.95 (3H, s, OCH_3), 4.65−4.70 (1H, m, OH), 5.06 (1H, q, J = 6.6 Hz, CH), 5.48 (5H, s, Cp), 6.11 (1H, t, J = 5.9 Hz, Ar−H), 6.21(1H, t, J = 5.9 Hz, Ar−H), 6.47 (1H, d, J = 5.9 Hz, Ar−H), 6.51 (1H, d, J = 5.9 Hz, Ar−H); IR (Nujol) 3580, 837 cm^{-1}. Anal. Calcd for $C_{14}H_{17}O_2PF_6Ru$: C, 36.29; H, 3.70. Found: C, 36.15; H, 3.58.

Preparation of Complex 3 by $NaBH_4$ Reduction. To a solution of *o*-methoxyacetophenone ruthenium complex **4** (70 mg, 0.15 mmol) in a mixture of THF (3.0 mL) and MeOH (3.0 mL) was added $NaBH_4$ (12.0 mg, 0.30 mmol) at 25 °C under argon. The resulting solution was stirred for 3 h and quenched with saturated NH_4Cl (1.0 mL). The reaction mixture was filtered off, and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel chromatography with CH_2Cl_2/acetone to give the inseparable 1:2 diastereomer mixture of ruthenium complexes **2** and **3** (68 mg, 98%). Major diastereomer, complex **3**: ^{1}H NMR (270 MHz, acetone-d_6) δ 1.55 (3H, d, J = 6.3 Hz, CH_3), 3.95 (3H, s, OCH_3), 4.75 (1H, d, J = 5.7 Hz, OH), 4.96−5.00 (1H, m, CH), 5.52 (5H, s, Cp), 6.08−6.36 (1H, m, Ar−H), 6.46−6.51(1H, m, Ar−H), 6.47 (1H, d, J = 5.7 Hz, Ar−H), 6.58 (1H, d, J = 5.7 Hz, Ar−H).

Diastereoselective Ruthenium Complexation: Preparation of Complex 6a. A solution of *o*-methoxy-α-methylbenzyl alcohol **5a** (63 mg, 0.41 mmol) and $[CpRu(CH_3CN)_3]PF_6$ (60 mg, 0.14 mmol) in dry 1,2-dichloroethane (14.0 mL) was degassed by three freeze/vacuum/thaw cycles and refluxed for 20 h under argon. The reaction mixture was filtered off, and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel chromatography with CH_2Cl_2/acetone to give the ruthenium complex **6a** (176 mg, 93%) as colorless crystals: mp 135 °C; ^{1}H NMR (270 MHz, acetone-d_6) δ 1.45 (3H, d, J = 6.6 Hz, CH_3), 3.95 (3H, s, OCH_3), 4.77 (1H, m, OH), 5.06 (1H, q, J = 6.6 Hz, CH), 5.48 (5H, s, Cp), 6.11 (1H, t, J = 5.9 Hz, Ar−H), 6.21(1H, t, J = 5.9 Hz, Ar−H), 6.47 (1H, d, J = 5.9 Hz, Ar−H), 6.51 (1H, d, J = 5.9 Hz, Ar−H); IR (Nujol) 3580, 837 cm^{-1}. Anal. Calcd for $C_{14}H_{17}O_2PF_6Ru$: C, 36.29; H, 3.70. Found: C, 36.15; H, 3.58.

Preparation of Compound 9a. To a solution of (*S*)-oxazaborolidine (37 mg, 0.13 mmol) and borane methyl sulfide complex (0.08 mL, 0.81 mmol) in THF (10 mL) was added a solution of the ketone compound **8a** (243 mg, 0.67 mmol) in THF (20 mL) at room temperature under argon. The resulting solution was stirred for 15 min, quenched with water, and extracted with EtOAc. The extract was washed with brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography to give optically active alcohol **9a** (240 mg, 99%, 95% ee) as a colorless oil: $[\alpha]_D^{21}$ 9.3 (*c* 1.12, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.42 (3H, d, J = 6.3 Hz, CH_3), 2.45 (3H, s, CH_3), 3.08 (1H, brs, OH), 3.77 (3H, s, OCH_3), 4.76 (1H, q, J = 6.3 Hz, CH), 6.91 (1H, d, J = 8.2 Hz, Ar−H), 7.17 (1H, dd, J = 8.2, 1.6 Hz, Ar−H), 7.18 (1H, d, J = 1.6 Hz, Ar−H), 7.25 (1H, t, J = 7.6 Hz, Ar−H), 7.35 (1H, dd, J = 7.6, 1.6 Hz, Ar−H), 7.75 (1H, dd, J = 7.6, 1.6 Hz, Ar−H); IR ($CHCl_3$) 3050, 1520, 1280 cm^{-1}; MS (relative intensity) *m*/*z* 364 (M^+, 15), 197 (100), 169 (10), 150 (11), 118 (2), 43 (3); HRMS calcd for $C_{17}H_{17}O_4Br$ 364.0306, found 364.0308. Optical purity was determined by HPLC with Chiralpak AS: eluted with *n*-hexane/2-propanol (9:1); flow rate 1 mL/min; temperature 40 °C; retention time, 10.3 min (*R*-isomer) and 11.5 min (*S*-isomer).

Pd-Catalyzed Coupling Reaction: Preparation of Compound 10a. A mixture of the optically active alcohol **9a** (200 mg, 0.55 mmol), $Pd(OAc)_2$ (12 mg, 0.055 mmol), 2-(di-*tert*-butylphosphino)biphenyl (33 mg, 0.11 mmol, 20 mol %), and sodium acetate (90 mg, 1.1 mmol) in dry DMA (7.0 mL) was degassed and stirred at 100 °C for 5.5 h under argon. The solvent was extracted with EtOAc. The extract was washed with brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography with EtOAc/hexane to give the coupling product **10a** (108 mg, 69%): mp 157 °C; ^{1}H NMR (270 MHz, $CDCl_3$) for major diastereomer δ 1.10 (3H, d, J = 5.9 Hz, CH_3), 2.01 (1H, brs, OH), 2.65 (3H, s, CH_3), 3.99 (3H, s, OCH_3), 5.15 (1H, q, J = 5.9 Hz, CH), 7.14 (1H, d, J = 8.6 Hz, Ar−H), 7.51 (1H, m, Ar−H), 7.64 (1H, d, J = 7.6 Hz, Ar−H), 8.20 (1H, d, J = 7.6 Hz, Ar−H); for minor diastereomer δ 1.84 (3H, d, J = 5.9 Hz, CH_3), 2.01 (1H, brs, OH), 2.46 (3H, s, CH_3), 3.99 (3H, s, OCH_3), 5.15 (1H, m, CH), 7.12 (1H, d, J = 8.6 Hz, Ar−H), 7.51 (1H, m, Ar−H), 7.64 (1H, d, J = 7.6 Hz, Ar−H), 8.20 (1H, d, J = 7.6 Hz, Ar−H); IR ($CHCl_3$) 3000−3600, 1560, 1200 cm^{-1}. Anal. Calcd for $C_{17}H_{15}O_4$: C, 71.81; H, 5.67. Found: C, 71.61; H, 5.43.

Diastereoselective Ru-Complexation Reaction: Preparation of Compound 11a. A mixture of the coupling product **10a** (145 mg, 0.51 mmol) and $[CpRu(CH_3CN)_3]PF_6$ (200 mg, 0.46 mmol) in dry 1,2-dichloroethane (20 mL) was degassed by three freeze/vacuum/thaw cycles and refluxed for 30 min under argon. The reaction mixture was filtered off, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography with dichloromethane/hexane to give ruthenium complex **11a** (139 mg, 51%) as colorless crystals: mp 200 °C; $[\alpha]_D^{20}$ −24.2 (*c* 0.67, CH_2Cl_2); ^{1}H NMR (270 MHz, acetone-d_6) δ 1.24 (3H, d, J = 6.6 Hz, CH_3), 2.83 (3H, s, CH_3), 4.11 (3H, s, OCH_3), 5.10 (1H, q, J = 6.6 Hz, CH), 5.45 (1H, brs, OH), 5.57 (5H, s, Cp), 6.43 (1H, d, J = 6.3 Hz, Ar−H), 6.91 (1H, d, J = 6.3 Hz, Ar−H), 7.74 (1H, t, J = 7.6 Hz, Ar−H), 7.87 (1H, d, J = 7.6 Hz, Ar−H), 8.13 (1H, d, J = 7.6 Hz, Ar−H); ^{13}C NMR (68 MHz, acetone-d_6) δ 19.0, 23.9, 27.7, 40.5, 54.6, 58.5, 65.3, 70.7, 79.5, 82.1, 85.2, 111.2, 124.4, 125.7, 129.2, 130.9, 131.2, 139.6, 166.5, 176.6, 205.3; IR (Nujol) 3410, 1740, 1290 cm^{-1}. Anal. Calcd for $C_{22}H_{21}O_4PF_6Ru$: C, 44.39; H, 3.55. Found: C, 44.60; H, 3.68.

Stereoselective Ring Opening Reaction: Preparation of Compound 12a. To a solution of ruthenium complex **11a**

(40 mg, 0.067 mmol) in MeOH (11 mL) was added CH_3ONa (3.6 mg, 0.067 mmol) under argon, and the mixture was stirred for 15 min. The reaction mixture was concentrated under reduced pressure. The residue was diluted with acetone, and the precipitate was filtered off. The filtrate was concentrated under reduced pressure to give product **12a** (42 mg, 99%) as a colorless oil: $[\alpha]_D^{20}$ 67.3 (*c* 0.45, CH_2Cl_2); ^{1}H NMR (270 MHz, acetone-d_6) δ 1.59 (3H, d, J = 6.6 Hz, CH_3), 2.22 (3H, s, CH_3), 3.28 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 4.72 (1H, q, J = 6.6 Hz, CH), 5.11−5.16 (1H, m, OH), 5.23 (5H, s, Cp), 5.51 (1H, brs, OH), 5.81 (1H, d, J = 5.6 Hz, Ar−H), 6.01 (1H, d, J = 5.6 Hz, Ar−H), 7.39 (1H, t, J = 4.6 Hz, Ar−H), 7.50 (1H, d, J = 4.6 Hz, Ar−H), 7.70 (1H, d, J = 4.6 Hz, Ar−H); ^{13}C NMR (68 MHz, acetone-d_6) δ 22.5, 24.2, 37.6, 42.3, 52.2, 54.8, 67.0, 70.7, 72.7, 80.3, 98.7, 108.0, 121.0, 122.1, 128.9, 129.2, 131.1, 133.9, 135.2, 137.4, 167.8, 185.5, 205.0; IR (Nujol) 2890, 1710, 1290 cm^{-1}; MS (relative intensity) *m*/*z* 483 ($M^+ - PF_6$, 100); HRMS calcd for $C_{23}H_{25}O_5Ru$ ($-PF_6$) 483.0745; found 483.0747.

Preparation of Compound 13a. A solution of the ruthenium complex **12a** (40 mg, 0.064 mmol) in CH_3CN (40 mL) was exposed to a Hg lamp for 2 h. The solvent was removed under reduced pressure, and the residue was diluted with ethyl acetate and extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography with EtOAc/hexane to give the coupling product **13a** (20 mg, 96%): mp 138−139 °C; $[\alpha]_D^{19}$ 21.8 (*c* 0.52, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.38 (3H, d, J = 6.3 Hz, CH_3), 1.99 (3H, s, CH_3), 3.23 (1H, brs, OH), 3.70 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 4.39 (1H, q, J = 6.3 Hz, CH), 5.42 (1H, s, OH), 6.95 (1H, d, J = 8.6 Hz, Ar−H), 7.18 (1H, d, J = 8.6 Hz, Ar−H), 7.36 (1H, t, J = 7.6 Hz, Ar−H), 7.46 (1H, d, J = 7.6 Hz, Ar−H), 7.74 (1H, d, J = 7.6 Hz, Ar−H); ^{13}C NMR (68 MHz, acetone-d_6) δ 20.2, 22.2, 52.4, 55.9, 66.0, 100.5, 110.1, 116.5, 127.3, 127.6, 131.1, 133.4, 135.7, 136.6, 138.4, 141.0, 145.4, 169.0; IR ($CHCl_3$) 3600, 1560, 1300, 1020 cm^{-1}; MS (relative intensity) *m*/*z* 316 (M^+, 11), 298 (88), 251 (100), 241 (74), 152 (18)115 (14); HRMS calcd for $C_{18}H_{20}O_5$ 316.1311, found 316.1316.

Computational Method. Geometry optimizations were carried out with B3LYP hybrid density functional theory using a 6-31G* (C, H, O) and LACVP[27] (Ru) basis sets with the Gaussian 98[28] and Jaguar V3.5 suite of programs.[29] One-point energy was determined at B3LYP/6-31++G**(CHO) and B3LYP/LACVP (Ru) levels of theory. Vibrational frequency analysis was performed on noncomplexed compounds by using B3LYP/6-31G* level calculations to confirm the stationary points as either minima (no imaginary frequency) or transition structures (only one imaginary frequency). This analysis was performed for all Ru-cyclopentadienyl complexes by using the RHF/3-21G* level because of the excessive computational cost. The calculated frequencies were also used to determine zero-point vibration and therml energy, which were used as a zero-point correction for the electronic energies calculated at B3LYP/6-31G*(LACVP*) and higher level calculations.

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Supporting Information Available: Experimental procedures and characterization data of products and X-ray analysis of **6a**, **11a**, **16**, **17**, **18**, and **27**. This material is available free of charge via the Internet at http://pubs.acs.org.

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