Transition-Metal Aqua Complexes of 4,6-Dibenzofurandiyl-2,2′-bis(4-phenyloxazoline). Effective Catalysis in Diels−Alder Reactions Showing Excellent Enantioselectivity, Extreme Chiral Amplification, and High Tolerance to Water, Alcohols, Amines, and Acids

Shuji Kanemasa,*,† Yoji Oderaotoshi,† Shin-ichi Sakaguchi,† Hidetoshi Yamamoto,† Junji Tanaka,† Eiji Wada,† and Dennis P. Curran‡

Contribution from the Institute of Advanced Material Study, Kyushu University, Kasugakoen, Kasuga 816, Japan, and Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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Abstract: Cationic aqua complexes are prepared from a trans-chelating tridentate ligand, (*R*,*R*)-4,6-dibenzofurandiyl-2,2′-bis(4-phenyloxazoline) (DBFOX/Ph), and various transition-metal(II) perchlorates. These complexes are effective catalysts in the Diels−Alder reactions of cyclopentadiene with 3-alkenoyl-2-oxazolidinone dienophiles and show excellent enantioselectivities. The active catalyst complex prepared from nickel(II) perchlorate hexahydrate has an octahedral structure with three aqua ligands, and it can be isolated and stored for months without loss of catalytic activity. Iron(II), cobalt(II), copper(II), and zinc(II) complexes are similarly active. The absolute configuration induced in the reaction can be readily predicted on the basis of the C_2-symmetric structure of the complexes as well as the simple structure of the substrate complex. The aqua complex prepared from Ni(II) or Zn(II) perchlorate results in highly effective chiral amplification in the Diels−Alder reaction. Use of the DBFOX/Ph ligand of a low enantio purity of 20% ee leads to a 96% ee for the endo cycloadduct. Two mechanisms for amplification are involved in this remarkable chiral amplification: (1) precipitation of an S_4-symmetric meso 2:1 complex between DBFOX/Ph and Ni(II) ion and (2) associative formation of 1:1 heterochiral complexes by the aid of hydrogen bonds based on aqua ligands to produce stable meso oligomers.

Introduction

Exploration of effective chiral catalysts is essential in asymmetric synthesis. High catalytic activity and induction of high enantioselectivity in catalyzed reactions are probably the most important subjects in this field. Although many examples have been reported of chiral Lewis acid catalysts that show effective catalytic activity resulting in high enantioselectivities, there are some other features of catalytic processes that remain to be improved. One undesirable but inevitable nature of catalyst complexes is the formation of oligomeric aggregation, which often affects the catalytic activity.[1] Accordingly, appropriate structural design to avoid such aggregation is a worthwhile goal; monomeric structures of catalysts would lead to enhanced catalytic activity. The second desirable characteristic is the stability of catalyst complexes; the assistance of protic media such as water, alcohols, acids, and amines is highly beneficial. Lability in protic media is usually observed for traditional Lewis acid catalysts, restricting their use in catalyzed asymmetric reactions under protic conditions.

Cis-chelating ligands have been used frequently for the chiral modification of Lewis acid catalysts. In cis complexes, the metallic center tends to be exposed to the undesirable access of other molecules of the ligand and the complex itself. Oligomer formation becomes easy, and this usually occurs. Our idea to avoid this aggregate formation involves the employment of a tridentate trans-chelating ligand. The use of neutral ligands such as bisoxazoline types[2−14] seems to be favorable for the following reasons: (1) Coordination of three anionic ligands to a metallic center will reduce the Lewis acidity of the metallic center. The combination of neutral tridentate

† Kyushu University.

‡ University of Pittsburgh.

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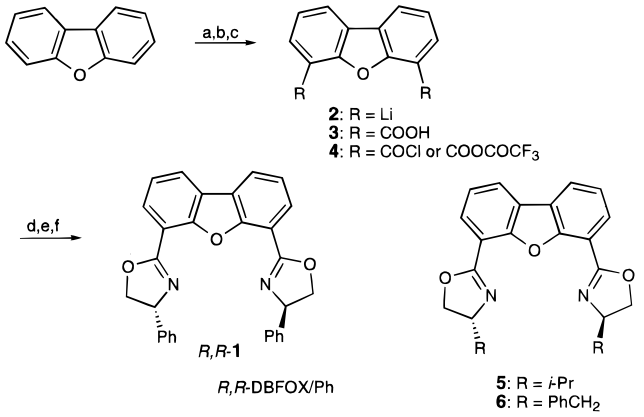
ligands with noncoordinating anionic ligands produces cationic complexes which may maintain a high catalytic activity. (2) Competitive coordination between a chiral ligand and a substrate is generally a challenging problem; if the substrate completely displaces the chiral ligand, an achiral catalyst can result. Tridentate ligands are expected to increase the stability of the complex structure with respect to ordinary bidentate ligands. (3) We have learned from molecular modeling inspection that the trans-chelating structure of two oxazoline moieties, especially when these two heterocyclic rings are coplanar, provides an attractive chiral space around the metallic center. Some effective enantioselectivity is anticipated in the catalyzed reactions. (4) The metal included in the above model complex is located in the middle of the chiral structure surrounded by the chiral ligands, so that aggregation is disfavored. However, despite these attractive features, there are only a few examples of effective catalysts that bear trans-chelating tridentate ligands.[12,15−17]

Homogeneous catalysts including transition metals of low oxidation levels have been used as Lewis acid catalysts. Pioneering work by Bosnich and co-workers has recently unveiled a new category of transition-metal Lewis acid catalysts. Some aqua complexes of titanium[18] and ruthenium[19] salts are highly air-stable and water-tolerant. These show high catalytic activity and effective turnover numbers of the catalytic cycle in Diels−Alder reactions of α,β-unsaturated carbonyl dienophiles. This suggests that the aqua ligands can be very rapidly replaced with dienophiles even in the presence of additional water.[19] An enantiopure titanium catalyst with aqua ligands, as well as some anhydrous titanium and zirconium complexes,[20] has achieved reasonable enantioselectivities.[18a]

Scheme 1[a]



[a] (a) *n*-BuLi in THF at −40 °C → room temperature → reflux; (b) poured onto dry ice and acidified (44%); (c) $SOCl_2$ in CF_3COOH, reflux for 3 h, then excess $SOCl_2$ removed; (d) (*R*)-phenylglycinol−Et_3N in $CHCl_3$ at room temperature for 24 h; (e) $SOCl_2$ at room temperature for 3 h; (f) aqueous NaOH in MeOH−$CHCl_3$ at room temperature for 24 h (63% based on the dicarboxylic acid).

In this report, we present a new class of trans-chelating tridentate ligands, (*R*,*R*)-4,6-dibenzofurandiyl-2,2′-bis(4-phenyloxazoline) (DBFOX/Ph).[21] The cationic aqua complexes prepared from this enantiopure ligand and various transition-metal(II) perchlorates induce absolute enantioselectitivity in the Diels−Alder reactions of 3-alkenoyl-2-oxazolidinone dienophiles. The complex of $Ni(ClO_4)_2{\cdot}6H_2O$, which has an octahedral structure with three aqua ligands, is isolable and can be stored in air for months without loss of catalytic activity. Iron(II), cobalt(II), copper(II), and zinc(II) complexes are similarly active. Aqua complexes of Ni(II) or Zn(II) perchlorate induce effective chiral amplification in the Diels−Alder reactions in which a DBFOX/Ph ligand of 20% ee results in 96% ee for the endo cycloadduct. Two mechanisms for amplification are involved: (1) the S_4-symmetric meso 2:1 complex between DBFOX/Ph and Ni(II) is irreversibly formed and precipitates out of the solution, and (2) heterochiral 1:1 complexes are highly stabilized by oligomerization based on hydrogen bonds of aqua ligands. Homochiral complexes have some structural disadvantages.

Synthesis of DBFOX Ligands

Synthesis of (*R*,*R*)-4,6-dibenzofurandiyl-2,2′-bis(4-phenyloxazoline) (*R*,*R*)-**1**, DBFOX/Ph) starts with the known bislithiation[22] at the 4- and 6-positions of the commercially available dibenzofuran (Scheme 1). The lithiated intermediate **2** is dicarboxylated with dry ice to give 4,6-dibenzofurandicarboxylic acid (**3**, 44% based on dibenzofuran), which is sparingly soluble in most organic solvents. Conversion of **3** to the corresponding acid chloride **4** was very difficult under normal conditions of acid chloride preparation because of its low solubility. Indeed, treatment of **3** with either thionyl chloride in chloroform under reflux or refluxing with thionyl chloride without solvent was ineffective, and the starting acid **3** was quantitatively recovered unchanged. However, we found in the process of surveying reaction solvents that **3** is soluble in trifluoroacetic acid with a color change to deep violet. Accordingly, the carboxylic acid

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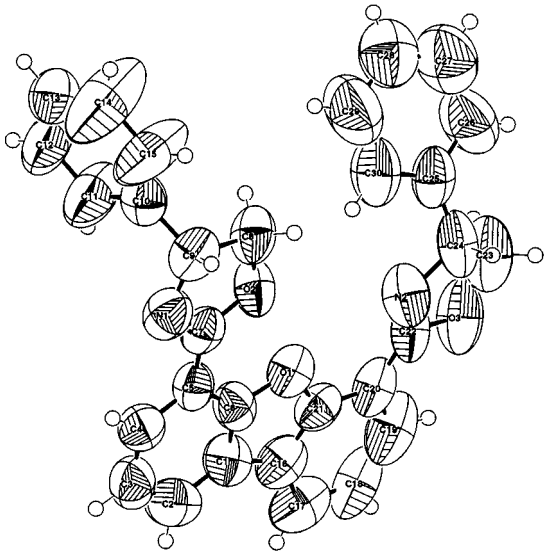


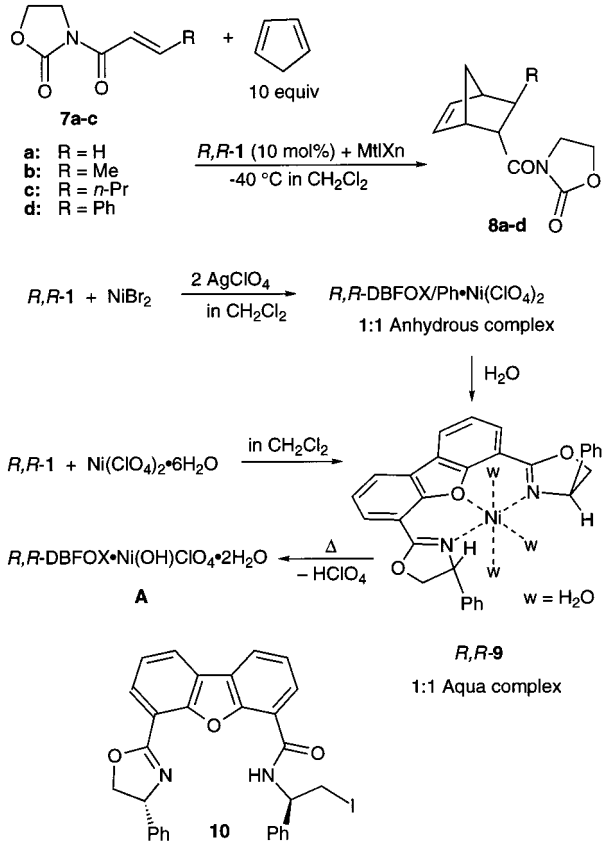
Figure 1. X-ray determined structure of 4,6-dibenzofurandiyl-2,2′-bis(4-phenyloxazoline) (*R*,*R*)-**1**.

3 was treated under reflux with thionyl chloride in the presence of trifluoroacetic acid.[23] Removal of the excess thionyl chloride was followed by treatment with (*R*)-2-phenyl-2-aminoethanol to give the corresponding amide. The usual cyclization procedure including a sequence of chlorination of the hydroxyl group to a chloroethyl moiety and cyclization by the aid of sodium hydroxide gave (*R*,*R*)-**1** in 63% yield for the total steps starting from dicarboxylic acid **3**.

Other ligands having isopropyl (DBFOX/*i*-Pr, **5**) and benzyl (DBFOX/Bn, **6**) shielding substituents at the 4-position of the oxazoline ring can be prepared by similar routes. The DBFOX/Ph ligand (*R*,*R*)-**1** thus prepared was found to have an enantiomeric purity of 98.3% ee by HPLC using a chiral column (Daicel Chiralcel OD-H with hexane−*i*-PrOH, 9:1 v/v, 1 mL/min, $t(R) = 23.7$ min, $t(S) = 27.4$ min). The ligand (*R*,*R*)-**1** with this enantiomeric purity is suitable in the following asymmetric reactions.[24] Although attempted purification by crystallization forms a film on the wall of the flask, crystallization from ethyl acetate−hexane gives small crystals. X-ray diffraction analysis shows that two chiral 4-phenyloxazoline rings of **1** are attached to the 4- and 6-positions of the dibenzofuran skeleton so that the minimum distance between these two nitrogens can be 4.1 Å (Figure 1).[25]

In the Cambridge Structural Database there are 1322 examples of metal complexes which contain the imine nitrogen−nickel bond. Atomic distances for the nitrogen−nickel atom bond range from 1.8 to 2.2 Å with peaks at 1.90 and 2.05 Å.[26] Since the ionic radius of Ni(II) ion is 0.83 Å if it carries six ligands,[27] other metal ions having comparable ionic radii should fit between the two nitrogen atoms of the DBFOX/Ph ligand. When an appropriate metal ion is incorporated, the two oxazoline rings and the dibenzofuran ring of the DBFOX ligand lie in a plane and construct an ideal C_2-symmetric chiral structure.

Scheme 2



Catalyzed Asymmetric Diels−Alder Reactions

Magnesium Complexes. A variety of metal salts have been examined for the in situ formation of catalyst complexes from ligand **1**. The complexation procedure includes addition of an equimolar amount of ligand **1** to a suspension of a metal salt in dichloromethane. A clear solution results after stirring for a few hours at room temperature, indicating that the formation of the complex is complete. The resulting solution containing the catalyst complex was used to promote asymmetric Diels−Alder reactions between cyclopentadiene and 3-acryloyl-2-oxazolidinone (**7a**). Both the catalytic activity of the catalysts and levels of chirality induction were evaluated on the basis of the enantioselectivities observed for the endo cycloadduct **8a** (Scheme 2).

On the basis of the above analysis of ionic radii of metal ions, the magnesium ion (ionic radius 0.86 Å) was first selected. Lewis acid catalysts consisting of magnesium complexes are known, and oxazoline complexes have shown high catalytic activity.[7b,28] However, the DBFOX/Ph complexes prepared from $MgBr_2$, MgI_2, $Mg(OTf)_2$, MgI_2/I_2, or $MgBr_2/I_2$ showed only moderate to good enantioselectivities for *endo*-**8a** (Table 1, entries 1−5). In the last two cases, one of the anionic ligands bonded to magnesium ion was replaced with noncoordinating I_2Br^- or I_3^- counteranions. We expected to ensure two coordination sites on the cationic magnesium ion for the smooth

(23) Thionyl chloride and trifluoroacetic acid are known to produce trifluoroacetyl chloride and then trifluoroacetic anhydride. Therefore, the reactive acylating reagent involved in the present reaction would be the bis mixed anhydride, the bis acid chloride, or mixed types.

(24) A remarkable chiral amplification effect, observed in the Diels−Alder reactions catalyzed by the metal complexes of DBFOX/Ph•$Ni(ClO_4)_2$•-$3H_2O$, cancels the decrease of enantioselectivity by contamination by an enantioisomeric ligand (see the text).

(25) The authors have deposited atomic coordinates for the structures of (*R*,*R*)-**1**, (*R*,*R*)-**9**, *meso*-**22**, and (*R*,*R*)-**9**/(*S*,*S*)-**9** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

(26) The Cambridge Structural Database including 167 797 data (updated in 1997) was used.

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Table 1. Diels−Alder Reactions of Cyclopentadiene with 3-Acryloyl-2-oxazolidinone (**7a**) Catalyzed by DBFOX/Ph·Magnesium Ion Complexes

entry	metal salt[a]	cat./mol %	temp/°C	time/h	yield/%[b]	endo:exo[c]	ee/%[d]
1	$MgBr_2$	10	rt[e]	1	99	89:11	41
2	MgI_2	10	rt	2	89	91:9	70
3	$MgBr_2$, I_2	10	rt	1	96	90:10	69
4	MgI_2, I_2	10	−40	48	94	95:5	80
5	$Mg(OTf)_2$	10	rt	1	93	88:12	25
6	$Mg(ClO_4)_2$	10	rt	1	quant	92:8	89
7	$Mg(ClO_4)_2$	10	−40	10	quant	97:3	91
8	$Mg(ClO_4)_2$	50	rt	0.5	quant	91:9	92
9	$Mg(ClO_4)_2$	100	rt	0.5	97	93:7	>99
10	$Mg(ClO_4)_2 + 3H_2O$	10	−40	48	68	96:4	48

[a] Catalysts were prepared in situ from DBFOX/Ph and a metal salt in dichloromethane. [b] Yield of isolated products. [c] Determined by ^1H NMR. [d] Optical purity of *endo*-**8a**: determined by HPLC (Chiralcel OD). [e] Room temperature.

Table 2. DBFOX/Ph·$Ni(ClO_4)_2$·$3H_2O$ Catalyzed Diels−Alder Reactions of Cyclopentadiene with 3-Alkenoyl-2-oxazolidinones **7a**−**c** Leading to Cycloadducts **8a**−**c**

entry	**7**	catalyst[a]	mol %	temp./°C	time/h	product **8**	yield/%[b]	endo:exo	ee/%[b]
1	**a**	DBFOX/Ph	10	rt[g]	2	**a**	95	92:8	89
2	**a**	DBFOX/Ph	10	−20	24	**a**	97	97:3	95
3	**a**	DBFOX/Ph	10	−40	14	**a**	96	97:3	>99
4	**a**	DBFOX/Ph	10	−78	96	**a**	quant	98:2	>99
5	**a**	DBFOX/Ph	2	−40	21	**a**	95	98:2	96
6	**a**	DBFOX/Ph	2	0	4	**a**	96	95:5	89
7	**a**	DBFOX/Ph	1	rt	1	**a**	95	92:8	78
8	**a**	**9**	10	−40	72	**a**	98	98:2	>99
9	**a**	**A**[c]	10	−40	72	**a**	quant	97:3	>99
10	**a**	**A**[d]	10	−40	48	**a**	quant	96:4	>99
11	**a**	MBOX/Ph **12**[e]	10	−40	72	**a**	97	88:12	−52
12	**b**	DBFOX/Ph	10	rt	20	**b**	90	92:8	93
13	**c**	DBFOX/Ph	10	rt	72	**c**	quant	93:7	94
14	**d**	DBFOX/Ph	10	rt	48	**d**	54	nd[h]	74

[a] Unless otherwise noted, catalysts were prepared in situ from a ligand and $Ni(ClO_4)_2$·$6H_2O$. [b] Enantiomeric purity of the endo cycloadduct *endo*-**8**. Determined by HPLC (Chiralcel OD). [c] Catalyst **A** was isolated by evaporation of the solvent. [d] Catalyst **A** was used after exposure to air for 3 months. [e] MBOX/Ph: (*R*,*R*)-Isopropylidene-2,2′-bis(4-phenyloxazoline) (**12**). [f] Anhydrous complex prepared from $NiBr_2$ and $AgSbF_6$. [g] Room temperature. [h] Not determined.

coordination of bidentate dienophile **6a**. Although an increase of catalytic activity was observed as expected, this was negated by decomposition of the complex: a red precipitate was produced over the course of reaction. This decomposition product was assigned to be *N*-iodoethylamide **10** (Scheme 2). When the magnesium ion is incorporated between the two nitrogen atoms of (*R*,*R*)-**1**, the imidate moiety is activated. Attack of the iodide at the 5-position slowly opens the oxazoline ring. The magnesium complex prepared in situ from the decomposition product **10** showed a low enantioselectivity (room temperature, 1 h, 99%, endo:exo = 90:10, 12% ee).

Accordingly, cationic complexes having less nucleophilic counteranions should be more favored, and $Mg(ClO_4)_2$ was selected. The cationic DBFOX/Ph complex of $Mg(ClO_4)_2$ is a better catalyst than $Mg(OTf)_2$[29] and provides 89% ee for *endo*-**8a** under comparable conditions. When a stoichiometric amount of $Mg(ClO_4)_2$ complex is used, a single enantiomer of *endo*-**8a** is produced even at room temperature (entry 9), indicating that the DBFOX/Ph ligand (*R*,*R*)-**1** provides a highly effective chiral space around the magnesium ion. Unfortunately, the catalytic activity is not high enough and the behavior is affected by the presence of water (entry 10).

Nickel Complexes. Nickel(II) perchlorate hexahydrate, Ni-$(ClO_4)_2$·$6H_2O$, is one of several metal perchlorates surveyed for the DBFOX/Ph−metal complexes. This perchlorate salt is totally insoluble in dichloromethane, but dissolves in the presence of DBFOX/Ph ligand. Surprisingly, the bluish green complex derived from commercially available $Ni(ClO_4)_2$·$6H_2O$, possessing six aqua ligands, exhibits a high catalytic activity. Diels−Alder reactions with 10 mol % of the aqua complex at −40 °C give a single enantiomer of *endo*-**8a** (Table 2, entry 3). Both the chemical yield and the endo:exo ratio are also excellent (96% yield, endo:exo = 97:3). High enantioselectivity remains with a catalytic loading of as little as 2 mol % of the nickel complex (96% ee). However, with a small catalytic loading, the reaction rate is too low to neglect an undesired effect from the uncatalyzed reaction.[30] With β-substituted dienophiles **7b**−**d**, which are much less reactive than the unsubstituted one **7a**, reactions were performed at room temperature (entries 12−14). The observed enantioselectivities of 93 and 94% ee, for the dienophiles **7b,c** having a primary alkyl substituent, are satisfactory for the conditions employed. However, the phenyl-substituted substrate **7d** shows rather a low chemical yield with a poor enantioselectivity even when the reaction is catalyzed by the anhydrous complex in situ prepared from (*R*,*R*)-**1**, $NiBr_2$, and $AgSbF_6$ (entry 14). Use of the aqua complex is less effective (room temperature, 72 h, 20%, 51% ee for *endo*-**8d**).

Although the ligand (*R*,*R*)-**1** is difficult to crystallize as mentioned above, the crystallization of the nickel complex is relatively easy. Thus, the anhydrous complex DBFOX/Ph·Ni-$(ClO_4)_2$ was crystallized from acetone−dichloromethane to give fine crystals of (*R*,*R*)-**9**. The X-ray stereostructure of **9**, shown in Figure 2,[25] indicates that the complex has a molecular formula of DBFOX/Ph·$Ni(ClO_4)_2$·$3H_2O$ with an octahedral structure. The two oxazoline rings are coplanar with the plane of

(29) Strong coordination of triflate ligands to the magnesium ion may be a reason for the poor catalytic activity (see ref 7d).

(30) Uncatalyzed Diels−Alder reactions of cyclopentadiene take place at room temperature: 80% of **8a** after 5 min with **7a**; 7% of **8b** after 3 h with **7b**.

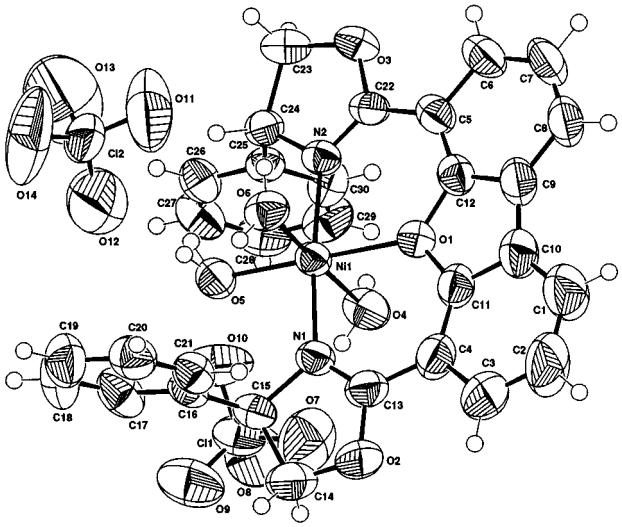


Figure 2. ORTEP drawing of DBFOX/Ph·$Ni(ClO_4)_2$.$3H_2O$ **9**.

bibenzofuran, forming a beautiful C_2-symmetric chiral structure. The nickel ion is bound to three water molecules and the furan oxygen atom. The N−Ni−N bond is almost linear (∠N−Ni−N = 174.2°), indicating that DBFOX/Ph **1** is trans-chelating toward Ni(II) ion.[31] The two N−Ni distances are 2.059 and 2.065 Å, which are typical of bond distances between an imine nitrogen and a nickel ion. To our great delight, the isolated crystal **9** was found to be an active catalyst in the Diels−Alder reaction leading to the absolute enantioselectivity for *endo*-**8a** at −40 °C (Table 2, entry 8).

Water-Tolerance of Catalysts. The catalyst **9** shows high water tolerance against moisture in air. Accordingly, we prepared the aqua complex **9** directly from the DBFOX/Ph ligand (*R*,*R*)-**1** and $Ni(ClO_4)_2$·$6H_2O$. Thus, a pale blue solid **A** can be isolated when $Ni(ClO_4)_2$·$6H_2O$ is treated with (*R*,*R*)-**1** in dichloromethane, followed by evaporation of the solvent. This solid **A** shows a high catalytic activity and enantioselectivity in the Diels−Alder reaction (−40 °C, quantitative, endo:exo = 97:3, >99% ee), and these attractive characteristics remained even after storage in air at room temperature for 3 months (Table 2, entries 9, 10). Although this complex **A** shows an IR spectrum almost identical to that of **9**, it has a hydroxo monoperchlorate complex structure on the basis of elemental analysis. The molecular formula of **A**, DBFOX/Ph·$Ni(ClO_4)$-(OH)·$2H_2O$, corresponds to a product formed by elimination of a perchloric acid from **9**.[32] We believe that the real active catalyst in reaction is diperchlorate trihydrate **9**, and that loss of perchloric acid leading to **A** occurred during the drying procedure. However, hydroxo monoperchlorate complex **A** also has a strong catalytic activity in the Diels−Alder reaction to show the absolute enantioselectivity (−40 °C, 48 h, 99%, endo:exo = 97:3, >99% ee).

Although the high catalytic activity of **9** is not affected by water, the enantioselectivity is modulated by the nature of the reaction solvent, cosolvent, and pretreatment. As shown in Table 3, the presence of 4A molecular sieves (MS 4A) did not improve the selectivity (89% ee at room temperature), but the preheating of $Ni(ClO_4)_2$·$6H_2O$ in vacuo with a heat gun prior to complexation was a useful modification (95% ee at room temperature).[33] The use of 3-acetyl-2-oxazolidinone as a model compound of dienophile **7a** in the complexation step increases the catalytic efficiency, while 1,2-dimethoxyethane is not effective (entries 3, 4). Choice of an appropriate reaction solvent is also important.[20b] For example, 1,2-dichloroethane is a better solvent than dichloromethane, but both dibromomethane and toluene are inferior (entries 7−9). Cosolvents such as ethyl ether or acetone improve the enantioselectivities (entries 5, 6). As will be discussed below, the 1:1 DBFOX/Ph·$Ni(ClO_4)_2$·-$3H_2O$ complex forms a weakly aggregated structure with a resulting decrease in catalytic activity. We believe that aqua ligands play an important role in this phenomenon. Weakly coordinating solvents or cosolvents would be replaced with the aqua ligands to dissociate the oligomeric aggregation. The solvent-coordinating monomeric complex shows a higher catalytic activity. Less coordinating or strongly coordinating additives are not effective. Replacement of the perchlorate counterion with less coordinating hexafluoroantimonate ions[34] was not helpful (entry 10).

Table 3. Effect of Solvent, Additive, Preparation of Catalyst, and Pretreatment in the Diels−Alder Reactions of Cyclopentadiene with 3-Acryloyl-2-oxazolidinone (**7a**)[a]

entry	solvent, additive, pretreatment	time/h	yield/%	endo:exo	ee/%[b]
1	MS 4A in CH_2Cl_2	1	97	93:7	89
2[c]	heat gun in CH_2Cl_2	1	95	95:5	95
3[d]	1,2-dimethoxyethane in CH_2Cl_2	0.5	quant	93:7	89
4[d]	3-acetyloxazolidinone in CH_2Cl_2	0.5	quant	92:8	95
5	solvent: CH_2Cl_2−(Et_2O, 4:1 v/v)	0.5	quant	93:7	95
6	solvent: CH_2Cl_2−acetone, 4:1 v/v	0.5	quant	93:7	94
7	solvent: dibromomethane	0.5	99	93:7	81
8	solvent: 1,2-dichloroethane	1	quant	93:7	93
9[e]	solvent: toluene	3	quant	91:9	50
10[f]	$NiBr_2$/$AgSbF_6$ (10:20 mol %)	17	quant	97:3	83

[a] Catalyst was prepared in situ from $Ni(ClO_4)_2$·$6H_2O$ and DBFOX/Ph (10 mol % each), and the Diels−Alder reaction was performed at room temperature. [b] Enantioselectivity for *endo*-**8a**. [c] Nickel salt $Ni(ClO_4)_2$.$6H_2O$ was heated with a heat gun in vacuo prior to complexation. [d] Catalyst was prepared by stirring $Ni(ClO_4)_2$.$6H_2O$, DBFOX/Ph, and an additive (10 mol % each) in dichloromethane followed by evaporation of the solvent. [e] Heterogeneous reaction. [f] At −40 °C.

Other Complexes. The red complex derived from Co-$(ClO_4)_2$·$6H_2O$ shows a similar catalytic activity as well as excellent stereoselectivities (Table 4, entry 11). To compare with the aqua complex, we prepared the anhydrous nickel and cobalt complexes by treatment of the DBFOX/Ph ligand with an equimolar amount of $NiBr_2$ or $CoBr_2$ in dichloromethane, followed by the action of 2 equiv of $AgClO_4$ (Scheme 2). It is interesting that the nickel and cobalt aqua complexes are even more effective, both for catalytic activity and for enantioselectivity, than the corresponding anhydrous complexes (entries 1, 2, 10, 11). Addition of 3 equiv of water to the anhydrous nickel complex recovers the catalytic efficiency; the effect of water and other additives will be discussed below. DBFOX/Ph complexes derived from manganese(II), iron(II), copper(II), and zinc(II) perchlorates, both anhydrous and "wet", exhibit high catalytic activities resulting in excellent enantioselectivities in the Diels−Alder reactions, where the "wet" catalysts were prepared by the addition of 3 equiv of water to the anhydrous catalysts. On the other hand, the DBFOX/Ph complexes of Fe-(III), Cu(I), Rh(III), Pd(II), Ag(I), and Sn(II) salts as well as

(31) The N−metal−N bond angles of the trans-chelating pybox complexes have been reported: pybox/*i*-Pr·$RhCl_3$ complex (∠N−Rh−N = 158.7°)[16b] and pybox/*i*-Pr·$Ru(CH_2{=}CH_2)Cl_2$ complex (∠N−Ru−N = 153.5°).[16e]

(32) The structural assignment of **A** was based on elementary analysis and the FAB-MS spectrum. In the presence of plenty of water under severe conditions, partial hydrolysis of the perchlorate salt of **9** takes place to produce **A**.

(33) TG/DTA analysis indicates that $Ni(ClO_4)_2$·$6H_2O$ starts to decompose at about 170 °C and is finally dehydrated to give NiO_2 at about 350 °C. This heating procedure would produce partly dehydrated nickel species.

(34) For the counterion effect in Diels−Alder reactions, see ref 7d.

Table 4. Comparison of Anhydrous and Aqua Complex Catalysts in the Diels−Alder Reactions of Cyclopentadiene with 3-Acryloyl-2-oxazolidinone (**7a**)[a]

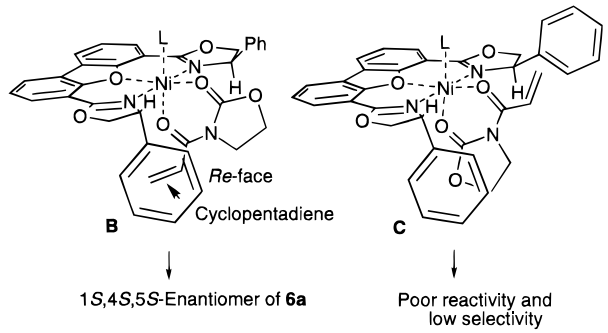
entry	metal salt[b]	temp/°C	time/h	yield/%	endo:exo	ee/%	IR/Å[c]
1	$Ni(ClO_4)_2$	−40	24	quant	95:5	96	0.83 (6)
2	$Ni(ClO_4)_2 \cdot 6H_2O$	−40	14	96	97:3	>99	
3	$Mn(ClO_4)_2$	−40	48	95	95:5	79	0.81 (6)
4	$Mn(ClO_4)_2 \cdot 6H_2O$	−40	96	96	97:3	83	
5	$FeCl_3$, I_2	rt[e]	1	98	90:10	37	0.69 (6)
6	$Fe(ClO_4)_3 \cdot nH_2O$ (n = 6−9)	rt	2	95	88:12	0	
7	$Fe(ClO_4)_3 \cdot nH_2O$ (n = 6−9)[d]	−40	11	91	94:6	67	
8	$Fe(ClO_4)_2$	−40	48	90	99:1	98	0.75 (6)
9	$Fe(ClO_4)_2 + 3H_2O$	−40	15	92	98:2	97	
10	$Co(ClO_4)_2$	−40	24	quant	97:3	93	0.79 (6)
11	$Co(ClO_4)_2 \cdot 6H_2O$	−40	48	97	97:3	99	
12	$Cu(OTf)_2$	−40	66	72	94:6	39	0.87 (6)
13	$Cu(ClO_4)_2$	−40	48	97	96:4	92	
14	$Cu((ClO_4)_2 + 3H_2O$	−40	15	99	97:3	96	
15	$Zn(OTf)_2$	rt	1	92	89:1	18	0.88 (6)
16	$Zn(ClO_4)_2$	−40	48	99	98:2	97	
17	$Zn(ClO_4)_2 + 3H_2O$	−40	15	99	96:4	97	
18	$Cr(ClO_4)_2 \cdot 6H_2O$	−40	96	52	96:4	20	0.87 (6)
19	$Ga(ClO_4)_3 \cdot 6H_2O$	−40	96	90	95:5	−10	0.76 (6)

[a] Catalyst: 10 mol %. [b] Catalysts were prepared in situ from DBFOX/Ph and the metal salts. Some anhydrous perchlorates were prepared in situ by treatment of the corresponding halides ($NiBr_2$, $FeCl_2$, $CoBr_2$, $CuCl_2$, ZnI_2) with $AgClO_4$. [c] Ionic radius with coordination number in parentheses (ref 27). [d] DBFOX/Ph, $Fe(ClO_4)_3 \cdot nH_2O$, and 3-acryloyl-2-oxazolidinone were treated with MS 4A prior to the Diels−Alder reaction. [e] Room temperature.

some lanthanoids are much less effective.[35] When the results observed in the Diels−Alder reactions using anhydrous and aqua complexes are compared, it is clear that the aqua complexes are again more fruitful in most cases. One exception is the iron(III) complex, which provides improved enantioselectivity when the catalyst is prepared in the presence of 3-acryloyl-2-oxazolidinone and MS 4A.

Transition-State Structure. On the basis of molecular modeling inspection of the possible transition-state structures of the (*R*,*R*)-**9**-catalyzed asymmetric Diels−Alder reaction, the *Re* face of the unsaturated bond of dienophile **7a** should be the enantioface participating in the catalyzed reaction. This prediction was verified by experiment: the absolute configuration and enantiomeric purity of *endo*-**8a** were determined by optical rotation and chiral HPLC analysis (Daicel Chiracel OD with hexane−2-PrOH, 99:1 v/v), respectively. The assigned structure of *endo*-**8a** is (1*S*,2*S*,4*S*)-3′-(bicyclo[2.2.1]hept-5-en-2-yl)-2′-oxazolidinone. We propose that the reacting catalyst−substrate (dienophile) complex between (*R*,*R*)-**7** and **7a** is a square bipyramidal structure containing an octahedral nickel ion.[36] Although there is evidence for the existence of two coordination structures, **B** and **C** in solution, the sterically more hindered or π-stacking **C** should be less reactive than **B** (Scheme 3). Therefore, we suggest that complex **B** is responsible for the highly selective reaction on the *Re* face with respect to the α-carbon of the dienophile. This analysis of the transition-state structure is consistent with the observed absolute configuration of *endo*-**8a**. Coordination structures such as **B** and **C** are the only possible substrate complexes. This structural simplicity is an important advantage of DBFOX complexes over the traditional cis-chelating bisoxazoline ligands, where a number of possible substrate complexes make it difficult to analyze the transition-state structure.[7a,37]

Scheme 3



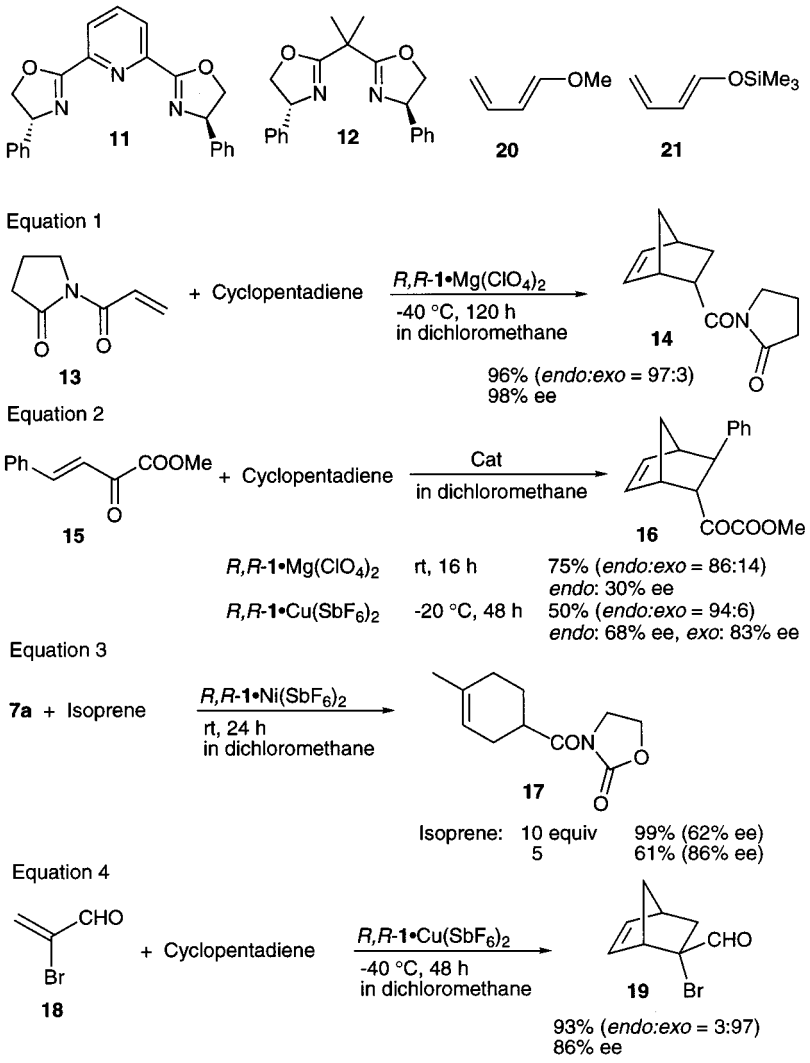
Competitive Coordination. In the substrate complexes, for example, **B** and **C** shown in Scheme 3, three kinds of ligands are coordinating onto the nickel ion: chiral DBFOX/Ph ligand (*R*,*R*)-**1**, chelating dienophile **7a**, and water. The first two should compete with each other, and this competition poses a general and serious problem in the reactions catalyzed by complexes of neutral chiral ligands. If substrate **7a** is a better ligand than chiral ligand **1**, then effective catalysis is not expected. The results suggest that **1** is a much better ligand than **7a** in this case. Formation of the tight complex is one of the most attractive features of tridentate DBFOX ligands. The nitrogen−nitrogen distance of 4.1 Å ensures the high stability of the nickel complex. As mentioned above, the solubility of $Ni(ClO_4)_2 \cdot 6H_2O$ in dichloromethane is very low in the absence of DBFOX/

(35) Diels−Alder reactions catalyzed by the DBFOX/Ph complex include the following metal salts. CuI/$AgClO_4$ (10:10 mol %/mol %): −40 °C, 96 h, 56%, 0% ee. $RhCl_3 \cdot 3H_2O$/$AgClO_4$ (10:30 mol %/mol %): −40 °C, 96 h, trace. $PdCl_2$/$AgClO_4$ (10:20 mol %/mol %): −40 °C, 96 h, trace. $PdCl_2(MeCN)_2$/$AgBF_4$ (10:20 mol %/mol %): room temperature, 2 h, 83%, endo:exo = 90:10, 0% ee. $AgClO_4$ (10 mol %): −40 °C, 96 h, 48%, 0% ee. $Sn(OTf)_2$ (10 mol %): room temperature, 2 h, 93%, endo:exo = 90:10, 0% ee. $CeCl_3$ (10 mol %): room temperature, 1 h, 91%, endo:exo = 90:10, 0% ee. $La(OTf)_3$ (10 mol %): room temperature, 1 h, 95%, endo:exo = 83: 17, 0% ee. $La(ClO_4)_3$ (10 mol %): room temperature, 1 h, 99%, endo:exo = 86:14, 0% ee. $Yb(ClO_4)_3$ (10 mol %): room temperature, 1 h, 94%, endo:exo = 89:11, 0% ee. $Gd(ClO_4)_3$ (10 mol %): room temperature, 1 h, 93%, endo:exo = 89:11, 0% ee.

(36) Formation of the 1:1 diastereomeric mixture of the catalyst−substrate (dienophile) complexes has been directly observed in the ^1H NMR spectral study (in CD_2Cl_2) using DBFOX/Ph·$Zn(ClO_4)_2$ and 3-acetyl-2-oxazolidinone, the octahedral coordinated structure being assigned as a reacting complex. The DBFOX/Ph·$Zn(ClO_4)_2$ complex does not undergo dissociation into components even in the presence of 3-acetyl-2-oxazolidine (Kanemasa, S.; Oderaotoshi, Y.; Tanaka, J.; Wada, E. Unpublished results).

(37) The $Ni(ClO_4)_2 \cdot 6H_2O$ complex of the 4-substituted isopropylidene-2,2′-bisoxazoline forms these two transition structures depending upon the steric nature of the 4-substituent (Kanemasa, S.; Oderaotoshi, Y.; Adachi, K. Unpublished results).

Scheme 4



Ph ligand **1**, and the dienophile **7a** itself does not solubilize the nickel ion at all. No rate acceleration is observed in the Ni(ClO$_4$)$_2$·6H$_2$O-catalyzed Diels−Alder reaction in the absence of **1**. Accordingly, excess amounts of Ni(ClO$_4$)$_2$·6H$_2$O can be employed in the reaction without loss of enantioselectivity; the amount of nickel ion necessary for the 1:1 complexation is extracted by the DBFOX/Ph ligand into solution. This will be discussed in detail in the section on chiral amplification. Such improved solubility is again no doubt due to the exceptionally high stability of the DBFOX/Ph·Ni(II) complex. On the other hand, nickel complexes of the known trans-chelating pybox/Ph ligand **11**,[16] both aqua and anhydrous complexes, show much lower selectivities.[38]

Diels−Alder reactions of other substrates can be catalyzed by the metal complexes of the DBFOX/Ph ligand (Scheme 4; catalysts: 10 mol % in all cases). Dienophiles such as *N*-acryloyl-2-pyrrolidinone (**13**) and methyl (*E*)-2-oxo-4-phenyl-3-butenoate (**15**) can be similarly activated with the magnesium complex to give the corresponding cycloadducts **14** and **16**, respectively, the former reaction giving an excellent enantioselectivity (eqs 1 and 2). Isoprene, a sluggish acyclic diene, reacts with dienophile **7a** in the presence of the anhydrous nickel catalyst, but the selectivity is not satisfactory (eq 3). Although 1-methoxy-1,3-butadiene (**20**) and 1-((trimethylsilyl)oxy)-1,3-butadiene (**21**) are expected in general to be more reactive dienes than cyclopentadiene, this expectation is not upheld in the reactions catalyzed by DBFOX complexes. The oxygen substituents at the 1-position of these dienes are sterically hindered by the plane of the dibenzofuran ring in the transition state. The monodentate dienophile 2-bromoacrolein (**18**) shows a high enantioselectivity in the reaction with cyclopentadiene when catalyzed by the copper(II) complex (eq 4).[39]

Effect of Solvents and Additives

Once high water tolerance becomes clear for the aqua complexes of DBFOX ligands with metal perchlorates, the next question is, How much water can be used without serious damage for the catalytic activity as well as enantioselectivity? We therefore examined the effect of added water in the catalyzed asymmetric Diels−Alder reactions. After addition of an appropriate amount of water to the anhydrous complex DBFOX/Ph·Ni(ClO$_4$)$_2$ which was prepared in the presence of dienophile

(38) Diels−Alder reactions catalyzed by the pybox/Ni(ClO$_4$)$_2$ complexes are as follows. Ni(ClO$_4$)$_2$·6H$_2$O (10 mol %): −40 °C, 144 h, 79%, endo:exo = 95:5, 2% ee. NiBr$_2$·AgClO$_4$ (10:20 mol %/mol %): −40 °C, 48 h, 95%, endo:exo = 87:13, 38% ee. We suspect, on the basis of the observed low catalytic activity as well as disappointingly low enantioselectivity, that the pybox ligand could not form a stable metal complex like the DBFOX/Ph ligand. The reason is not clear.

(39) Reactions catalyzed by nickel and zinc complexes are much less selective. NiBr$_2$/AgClO$_4$ (10:20 mol %/mol %): room temperature, 24 h, 91%, endo:exo = 6:94, 53% ee. ZnI$_2$/AgClO$_4$ (10:20 mol %/mol %): room temperature, 24 h, 91%, endo:exo = 6:94, 73% ee.

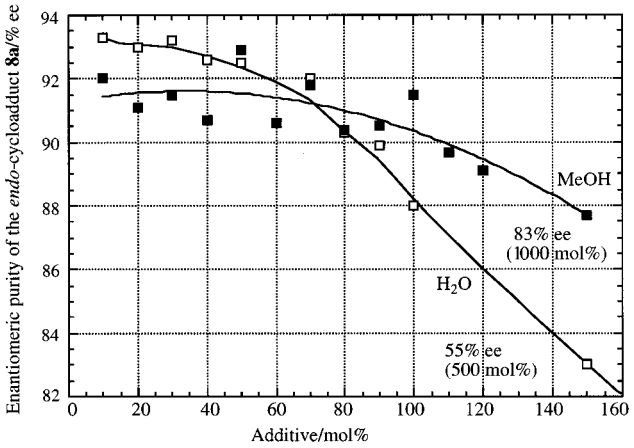


Figure 3. Relationship between the molar amount of additive and the enantiomeric purity observed for *endo*-**8a** in the Diels−Alder reaction between cyclopentadiene and **7a** catalyzed by (*R*,*R*)-DBFOX/Ph·Ni(ClO$_4$)$_2$ in dichloromethane at room temperature.

Table 5. Effect of Acid and Amine Additives in the DBFOX/Ph·Ni(ClO$_4$)$_2$ Catalyzed Diels−Alder Reactions of Cyclopentadiene with Dienophile **7a** at Room Temperature in Dichloromethane[a]

entry	additive	mol %	time/h	yield/%	endo:exo	ee/%
1	MeCOOH	10	0.7	84	97:3	91
2		60	0.7	92	91:9	88
3	PhCOOH	10	0.7	97	93:7	91
4		60	0.7	97	92:8	81
5	p-NO$_2$C$_6$H$_4$COOH	10	0.7	98	93:7	91
6	PhOH	60	0.7	98	94:6	92
7	PhNH$_2$	30	0.7	74	91;9	91
8	PhCH$_2$NH$_2$	30	0.7	46	94:6	90
9	pyridine	30	0.7	83	95:5	86
10	2,4,6-collidine	30	0.7	95	92:8	93
11	Et$_2$NH	30	1.2	75	90:10	1

[a] The anhydrous catalyst was prepared in situ by treatment of NiBr$_2$ and DBFOX/Ph (*R*,*R*)-**1** (10 mol % each) with Ag(ClO$_4$)$_2$ (20 mol %) in the presence of **7a**.

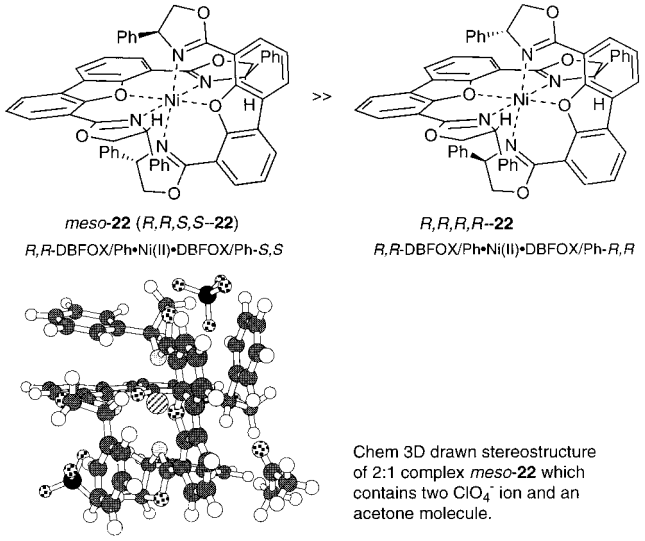
7a in dichloromethane, the reaction with an excess amount of cyclopentadiene was performed at room temperature. Enantioselectivity was as high as 93% ee for *endo*-**8a** up to 5 equiv of water added, and the satisfactory level of 88% ee was maintained when 10 equiv was added. However, enantioselectivity gradually decreases with increased amounts of water added: 83 and 55% ee from 15 and 50 equiv, respectively (Figure 3). When the reaction temperature goes down to −40 °C, an enantioselectivity as high as 98% ee results for up to 15 equiv of water additive. The effect of methanol at room temperature is quite surprising. In the presence of 15 and 100 equiv of methanol, the high enantioselectivities of 88 and 83% ee, respectively, are recorded for the reactions at room temperature.

The effects of a variety of acids and amines are summarized in Table 5. As long as amounts of these amine additives are limited to 3 equiv with respect to the catalyst (*R*,*R*)-**9**, high enantioselectivities can be obtained for *endo*-**8a**. The only exception is the reaction in the presence of diethylamine, where the cycloadduct **8a** was racemic.

Chiral Amplification

As mentioned above, DBFOX/Ph (*R*,*R*)-**1** is a tridentate ligand that coordinates strongly to nickel(II) perchlorate hexahydrate to form the characteristic planar structure with the molecular formula of DBFOX/Ph·Ni(ClO$_4$)$_2$·3H$_2$O (*R*,*R*)-**9**).[25] The three water ligands located at meridional positions may be replaced

Scheme 5



by another molecule of the DBFOX/Ph ligand if steric hindrance is negligible. On the basis of molecular model inspection, the heterochiral enantiomer (*S*,*S*)-**1** looks like a candidate to replace the water ligands to form the heterochiral 2:1 complex (DBFOX/Ph)$_2$·Ni(ClO$_4$)$_2$ ((*R*,*R*,*S*,*S*)-**22** or *meso*-**22**) (Scheme 5). However, the 2:1 complex containing a homochiral pair (*R*,*R*,*R*,*R*)-**22** can never be formed because of the severe steric hindrance between the 4-phenyl substituents of oxazoline rings. When a catalyst complex is prepared from DBFOX/Ph ligand **1** of a low enantiomeric purity, formation of the heterochiral 2:1 complex *meso*-**22** is expected, and it is expected that the resulting complex *meso*-**22** with saturated coordination should be inert in catalytic activity. If this happens, part of the minor enantiomer of the DBFOX/Ph ligand is consumed to enrich the enantiomeric purity of the remaining ligand, indicating a possibility of effective chiral amplification.[40−47] Accordingly, we have examined some experiments of chiral amplification in

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Table 6. Chiral Amplification Observed in the DBFOX/Nickel Hydrate Complex Catalyzed Diels−Alder Reactions between Cyclopentadiene and 3-Acryloyl-2-oxazolidine

		mol %								
entry	ligand[a,b] ee/%	metal[b]	ligand total	major	minor	excess[e]	time/h	endo[f]/%	yield/%	selectivity:[g] ee/%
1	20	10	10	6	4	2	72	98	99	91
2[h]	20	10	10	6	4	2	15	97	quant	94
3	20	20	20	12	8	4	72	97	95	96
4	20	20	10	6	4	2	72	96	95	85
5	20	10	20	12	8	4	72	94	quant	58
6	40	5	5	3.5	1.5	2	72	97	95	95
7	50	10	10	7.5	2.5	5	48	96	95	95
8	50	10	20	15	5	10	72	97	97	94
9	50	10	40	30	10	20	196	95	92	58
10	60	3.3	3.3	2.6	0.7	1.9	96	97	quant	94
11	80	2.2	2.5	2.2	0.3	1.9	72	97	97	96
12	80	10	10	9	1	8	48	96	95	98
13	80	10	20	18	2	16	72	98	quant	98
14	100	20	101	0	0	10	48	96	90	>99[h]

[a] Enantiomeric purity of ligand DBFOX/Ph. [b] Metal: $Ni(ClO_4)_2 \cdot 6H_2O$. Ligand: DBFOX. [c] Major enantiomer. [d] Minor enantiomer. [e] Mol % for the excess enantiomer of DBFOX/Ph. [f] Endo selectivity. [g] Determined by HPLC (Chiralcel OD). [h] The 1:1 complex catalysts (*R*,*R*)-**9** (6 mol %) and (*S*,*S*)-**9** (4 mol %) were used.

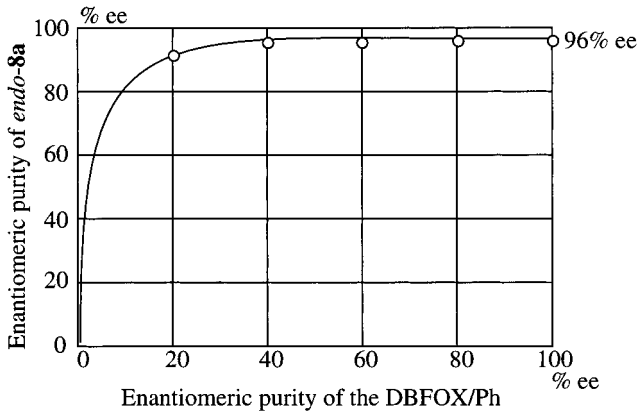


Figure 4. Chiral amplification in the reaction between cyclopentadiene and **7a** at −40 °C catalyzed by DBFOX/Ph + $Ni(ClO_4)_2 \cdot 6H_2O$ (excess enantiomer: 2 mol %).

the Diels−Alder reaction catalyzed by a complex between DBFOX/Ph and $Ni(ClO_4)_2 \cdot 6H_2O$.

A typical procedure is as follows: A catalyst was prepared in situ from $Ni(ClO_4)_2 \cdot 6H_2O$ (20 mol %) and DBFOX/Ph of a low enantiomeric purity (20% ee; (*R*,*R*)-**1**, 12 mol %; (*S*,*S*)-**1**, 8 mol %) with stirring in dichloromethane at room temperature for 2 h. During this procedure, the nickel salt becomes gradually dissolved in the solution, but at a late stage of this procedure some pale blue solid starts to precipitate. Without removal of this solid, the resulting suspension was employed in the Diels−Alder reaction between cyclopentadiene (10 equiv) and 3-acryloyl-2-oxazolidinone (**7a**) at −40 °C for 72 h. Cycloadduct **8a** was obtained in 95% yield (endo:exo = 97:3) with an enantioselectivity as high as 96% ee for *endo*-**8a** (Table 6, entry 3). Figure 4 shows the relationship between the enantiomeric purity of the DBFOX/Ph ligand used and the enantioselectivity observed for *endo*-**8a**, where the ratio of DBFOX/Ph versus $Ni(ClO_4)_2 \cdot 6H_2O$ is 1:1 mol/mol and the catalytic loading is 2 mol % for the excess enantiomer of **1**. With ligand **1** of 20% ee, a 91% ee was recorded for *endo*-**8a**, and a 95% ee was recorded from 40% ee ligand. One should recognize that excellent levels of chiral amplification have been attained, since the maximum enantioselectivity is 96% ee (*endo*-**8a**), which can be attained in the reaction using the pure enantiomer of DBFOX/Ph ligand (*R*,*R*)-**1** (2 mol %) at −40 °C. This means that the reaction has been catalyzed by the almost pure enantiomer of complex (*R*,*R*)-**7** which remained in the solution by an absolutely effective chirality enrichment process.

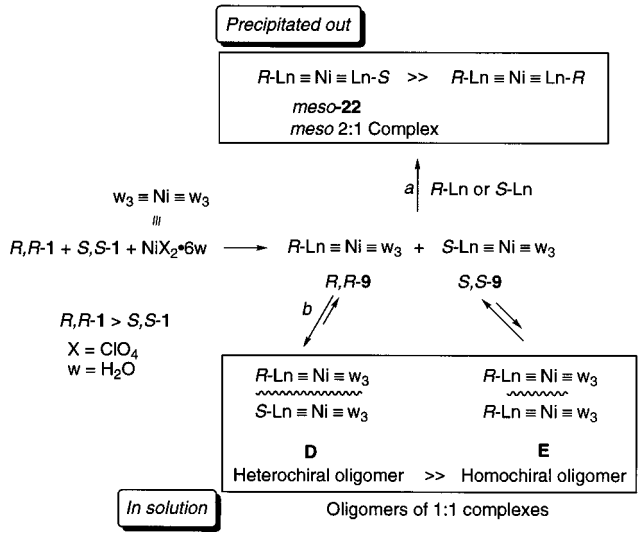
Meso 2:1 Complex Formation. Treatment of $Ni(ClO_4)_2 \cdot 6H_2O$ with the pure enantiomer of DBFOX/Ph ligand **1** produces the active 1:1 complex, which is soluble in dichloromethane at least at an early stage of complex formation.[48] When the ligand **1** of a low enantiomeric purity is used for complex formation, the pale blue solid **22** is rapidly precipitated regardless of the presence of dienophile **7**. The product **22** has a molecular formula of the monohydrate of $(DBFOX)_2 \cdot Ni(ClO_4)_2$ (by elemental analysis) consisting of a pair of heterochiral DBFOX/Ph ligands (*R*,*R*)-**1** and (*S*,*S*)-**1**. A CD spectrum recorded in 1,2-dichloroethane containing a small amount of DMSO shows no absorption. Accordingly, the structure can be assigned to be an S_4-symmetric meso structure. This unusual structure of *meso*-**22** was ultimately confirmed by X-ray single crystallography analysis as shown in Scheme 5.[49] The most straightforward access to *meso*-**22** is the treatment of 1:1 adduct (*R*,*R*)-**9** with the other enantiomer of free ligand (*S*,*S*)-**1**, and this actually takes place quantitatively.

The 2:1 complex *meso*-**22** is sparingly soluble in most organic solvents, but it has limited solubility in DMSO and DMF, which still show limited solubilities. No decomposition occurs even on heating in wet DMSO or DMF. Accordingly, once *meso*-**22** is formed in the step of complex formation, no dissociation into components, **1** and $Ni(ClO_4)_2 \cdot 6H_2O$, takes place, formation of *meso*-**22** being irreversible. *meso*-**22** is stable even in the presence of excess 3-acryloyl-2-oxazolidinone **7a** used as chelating reagent in the Diels−Alder reaction. The following experiments provide some supporting evidence for the inactivity of *meso*-**22**: (1) When the isolated 2:1 complex *meso*-**22** (4 mol %) is pretreated with a mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (16 mol %) and the pure enantiomer of (*R*,*R*)-**1** (2 mol %) in dichloromethane, a high chiral induction is recorded (97% ee for *endo*-**3**) in the Diels−Alder reaction at −40 °C. This selectivity is comparable to that observed in the reaction under the catalysis of 2 mol % of enantiomeric pure (*R*,*R*)-**1**. (2) The

(48) The 1:1 aqua complex **9** is soluble in dichloromethane, and the presence of dienophile **7** improves the solubility. Accordingly, no precipitate is formed when the complex formation is carried out with DBFOX/Ph and $Ni(ClO_4)_2 \cdot 6H_2O$ in the presence of dienophile **7**.

(49) The analysis was not completed because of the disorder of the acetone and the perchlorate ions. To solve this problem requires a spherical crystal and correction of absorption.

Scheme 6



Diels−Alder reaction is not accelerated by a mixture of the isolated *meso*-**22** (4 mol %) and the pure enantiomer of (*R*,*R*)-**1** (5 mol %).

By irreversible formation of *meso*-**22**, the major enantiomer of ligand **1** can be enriched in the solution so that the enantioselectivity for *endo*-**8a** should exceed the enantiomeric purity of the ligand **1** used (route a in Scheme 6). However, even when the complex formation is performed under reflux in 1,2-dichloroethane to effect the 2:1 complex formation ((*R*,*R*)-**1**, 12 mol %; (*S*,*S*)-**1**, 8 mol %; $Ni(ClO_4)_2 \cdot 6H_2O$, 10 mol %; 3 h), the yield of 2:1 complex *meso*-**22** was only 58%. The enantiomeric purity of **1** remaining in the solution is calculated to be 37% ee ((*R*,*R*)-**1**, 7.4 mol %; (*S*,*S*)-**1**, 3.4 mol %; $Ni(ClO_4)_2 \cdot 6H_2O$, 5.4 mol %), while the enantioselectivity actually observed for *endo*-**8a** was 88% ee. Apparently a chirality enrichment mechanism other than that through the precipitation of *meso*-**22** (route a) exists in the solution. We have not so far observed that the 1:1 complex **9** can be dissociated into each component under the usual reaction conditions. It is improbable that the 1:1 complex **9** as active catalyst undergoes disproportionation leading to the inert 2:1 complex *meso*-**22**. Accordingly, the formation of *meso*-**22** has to proceed only through the reaction of 1:1 complex **9** with free DBFOX/Ph ligand **1**, and hence this transformation is limited to occur in an early stage of complex formation. When all of the free ligand DBFOX/Ph **1** is consumed, the production of *meso*-**9** ceases.

When equiv amounts of $Ni(ClO_4)_2 \cdot 6H_2O$ and DBFOX/Ph are used in the catalyst preparation process, two molecules of ligand **1** are consumed to form heterochiral 2:1 complex *meso*-**22** so that $Ni(ClO_4)_2 \cdot 6H_2O$ becomes excess toward ligand **1** in the solution (entries 1−3, 7, 8, 11−13). The presence of excess free metal salt $Ni(ClO_4)_2 \cdot 6H_2O$ appears to be unfavorable since the competitive reaction catalyzed by achiral catalyst should affect the enantioselectivity of the reaction. However, the results indicate that this is not actually a serious problem. In the absence of DBFOX ligand **1**, $Ni(ClO_4)_2 \cdot 6H_2O$ is hardly soluble in dichloromethane.[50] This solubility advantage is supported by the following two observations: (1) No rate acceleration is observed in the Diels−Alder reaction catalyzed by $Ni(ClO_4)_2 \cdot 6H_2O$ in the absence of DBFOX/Ph ligand. Dienophile **7a** as chelating reagent cannot solubilize the nickel salt. (2) Even the reaction using excess $Ni(ClO_4)_2 \cdot 6H_2O$ together with the enantiopure (*R*,*R*)-**1** gives absolute enantioselectivity (entry 15). It is interesting that the use of excess ligand **1** leads to a decreased enantioselectivity for *endo*-**8a**, especially when the enantiomeric purity of **1** is low (entries 5, 6, 9, 14). This phenomenon is closely related with the chirality enrichment mechanism operating in the solution, as will be discussed below. In entry 9, where most of the metal salt has been consumed for the formation of inert meso-2:1 complex *meso*-**22**, only a little catalytic activity is expected.

Relative Stability of Two Oligomeric Forms of 1:1 Complexes. What is the second chirality enrichment mechanism operating in the solution? Most likely some heterochiral pairs of the 1:1 complex **9** are formed or they are further associated to form relatively stable racemic aggregation, while weak aggregation should result in the case of enantiopure 1:1 complex **9**. The aqua ligands apparently play an important role in the chirality enrichment process, increasing the stability of the associated heterochiral oligomers (route b in Scheme 2). For example, the Diels−Alder reaction using the anhydrous complex (20% ee, 10 mol %) prepared from DBFOX/Ph, $NiBr_2$, and $AgClO_4$ (1:1:2 molar ratio) only results in a low chiral amplification (entry 6, 23% ee for *endo*-**8**). When enantiopure 1:1 aqua complexes, (*R*,*R*)-**9** and (*S*,*S*)-**9**, are mixed in a ratio of 6 and 4 mol %, respectively, and used in the Diels−Alder reaction at room temperature, a 94% ee is observed for *endo*-**8a** (Table 6, entry 2). This indicates that the chiral enrichment mechanism working in the solution is much more effective.

In order to estimate the intermolecular interactions in homochiral and heterochiral aggregations of 1:1 complexes, the single crystals in each case were prepared. The X-ray structure of enantiopure 1:1 complex (*R*,*R*)-**9** is shown in Figure 2. On the other hand, single crystals of heterochiral pairs were prepared by the following procedure. Equivalent amounts of the enantiopure 1:1 complexes (*R*,*R*)-**9** and (*S*,*S*)-**9** were dissolved in dichloromethane containing acetone as cosolvent. After these two solutions were mixed, benzene was added. Slow evaporation of the relatively more volatile dichloromethane and acetone gave single crystals of the racemic 1:1 complex. In Figure 5 are depicted packing structures for the enantiopure 1:1 complex (*R*,*R*)-**9** and racemic compound (*R*,*R*)-**9**/(*S*,*S*)-**9**. Single crystals prepared from enantiopure 1:1 complexes (*R*,*R*)-**9** include four molecules of (*R*,*R*)-**9** in a unit cell, in which two each are parallel with a layer distance of 7.41 Å (Figure 5). We assume that intermolecular attractive interactions should be working through hydrogen bonds between the water ligands and perchlorate ions in the network. Measurement of the oxygen−oxygen distances between water ligand and perchlorate ion should be informative. However, the perchlorate ion has a spherical shape with high mobility so that the temperature factor for this anion is relatively big as shown in Figure 2. Accordingly, we used the distance between a chlorine atom of perchlorate and an oxygen atom of water to evaluate hydrogen bond interactions. We hypothesize that such an attractive interaction should exist when the distance is shorter than 4 Å. Each perchlorate ion is bonded with an equatorial and an axial water ligand of the same molecule of the 1:1 complex, and these axial waters are bonded with perchlorate ions which belong to the adjacent molecules (network A in Figure 5; the oxygen−chlorine distances are 3.91, 3.79, 3.75, 3.72, and 3.67 Å). As a result, the two adjacent 1:1 complexes (*R*,*R*)-**9** are linked with one hydrogen bond.

On the other hand, in the single crystals prepared from equiv amounts of heterochiral 1:1 complexes, (*R*,*R*)-**9** and (*S*,*S*)-**9**, a

(50) Comparison of the reaction rates in Diels−Alder reactions catalyzed by $Ni(ClO_4)_2 \cdot 6H_2O$ or under uncatalyzed conditions has been discussed in ref 21.

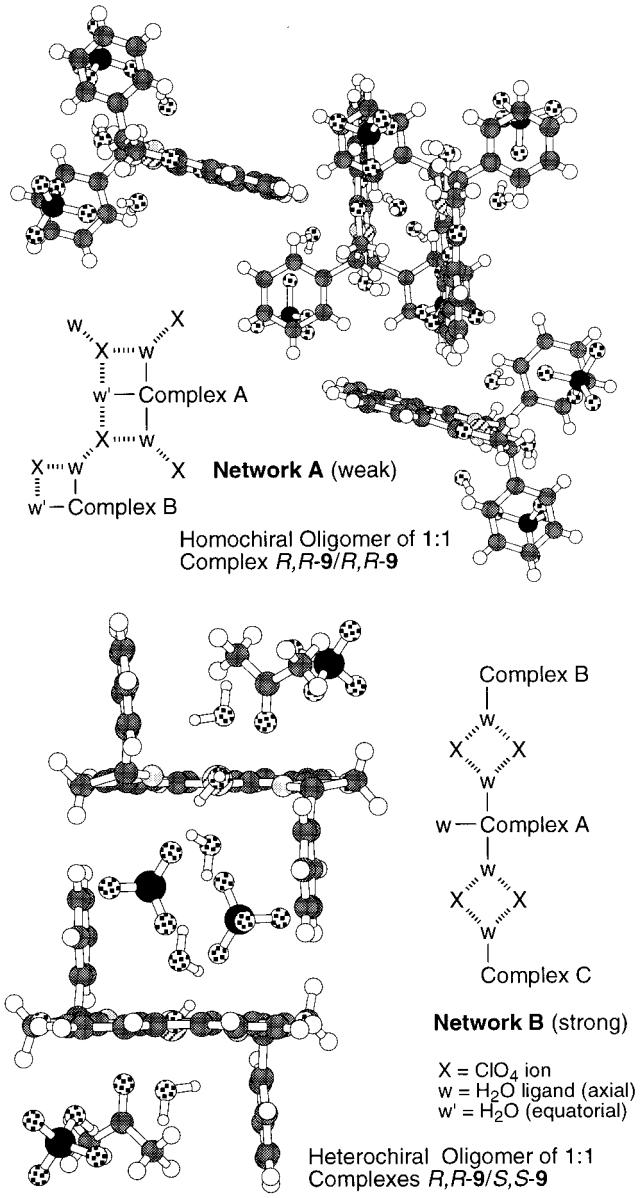


Figure 5. Packing structures containing four molecules of 1:1 complexes (*R*,*R*)-**9** (upper) and a pair of heterochiral 1:1 complexes (*R*,*R*)-**9** and (*S*,*S*)-**9** (lower).

pair of two heterochiral 1:1 complexes are incorporated in a unit cell to form a layered structure with alternate layer distances of 7.33 and 7.6 Å. Two perchlorate ions stay in the nallower gap, and two additional acetone molecules as crystallization solvent occupy the wider gap. The perchlorate ions interact with two axial water ligands by hydrogen bonds (3.71 and 3.77 Å) to construct a layered structure. The adjacent two molecules of heterochiral 1:1 complexes, (*R*,*R*)-**9** and (*S*,*S*)-**9**, interact with each other by two hydrogen bonds per one complex molecule. This suggests that heterochiral aggregation should be much stronger than the above homochiral case. We believe that the 1:1 complex (*R*,*R*)-**9** (supposed to be major enantiomer) would interact, even in the solution, with heterochiral 1:1 complex (*S*,*S*)-**9** much more strongly than homochiral 1:1 complex (*R*,*R*)-**9**. As a result, the minor complex is deactivated in the solution to enrich the major enantiomer of 1:1 complex (*R*,*R*)-**9**. This is the mechanism for effective chiral amplification occurring in the solution. Such a differential of the stabilization of oligomeric forms is supported by the following observation: Crystals of the enantiopure 1:1 complex rapidly dissolve in dichloromethane when treated with 3-acetyl-2-oxazolidine, while those of the racemic complex are not soluble even under harder conditions.

Solvent, Metal Ion, and Ligand Effects. The relative stability between homochiral and heterochiral aggregations of 1:1 complexes **9** should depend upon the polarity of solvents or additives used. We mentioned above that the addition of coordinating additives such as diethyl ether, acetone, and 1,2-dichloroethane works to activate the DBFOX complex catalyzed Diels−Alder reactions (Table 3). We therefore examined solvent and additive effects for chiral amplification. As seen in entries 1−3 of Table 7, 1,2-dichloromethane and diethyl ether, as solvent and additive, respectively, maintain high levels of amplification (compare with entry 5 of Table 6). This indicates that they solvate the 1:1 complexes to dissociate the weak homochiral oligomers of 1:1 complexes, but the heterochiral oligomers are still stable. On the other hand, a low level of chiral amplification results in the presence of acetone, meaning that acetone is powerful enough to dissociate the strong heterochiral oligomers. The effectiveness of hydrogen bonds of aqua ligands to SbF_6 anions is similar to the effectiveness of perchlorate ions (entry 5). Although aqua complexes of magnesium, iron(II), and copper(II) perchlorates are not proper choices for high chiral amplification, zinc perchlorate shows an even more effective amplification than nickel perchlorate (94% ee from 20% ee, entry 10). Thus, the complex is prepared from DBFOX/Ph (20% ee, 10 mol %) and ZnI_2 in dichloromethane, followed by treatment of $AgClO_4$ (20 mol %). After 3 equiv of water is added, the catalyst is used in the Diels−Alder reaction at −40 °C to give an enantiomeric activity of 96% ee (quantitative, endo:exo = 98:2) for *endo*-**3**. Thus, the absolute or theoretically maximum chiral amplification has been attained.

Conclusions

Cationic aqua complexes prepared from (*R*,*R*)-4,6-dibenzofurandiyl-2,2′-bis(4-phenyloxazoline) (called DBFOX/Ph) and metal(II) perchlorates such as magnesium, nickel, iron, cobalt, copper, and zinc ions show a high catalytic activity. They induce absolute enantioselectivity in the Diels−Alder reactions of cyclopentadiene with 3-alkenoyl-2-oxazolidinones. The DBFOX/Ph complex of $Ni(ClO_4)\cdot 6H_2O$ is isolated as a formula of DBFOX/Ph·$Ni(ClO_4)_2\cdot 3H_2O$, which can be stored in air for months without loss of catalytic activity. In some cases the aqua complexes are even more active than the anhydrous complexes. Alcohols, acids, and amines do not affect seriously the catalytic activity as well as the enantioselectivity. A remarkable chiral amplification is attained through two mechanisms: the irreversible formation of an insoluble meso 2:1 complex and hydrogen bond mediated oligomer formation among heterochiral enantiomers of 1:1 complexes.

Such exceptionally high stability, effective chiral control, and remarkable chiral amplification apparently depend upon the following new features: (1) the size-fitted tridentate cavity of the DBFOX ligand, (2) the trans-chelating structure bearing the metal ion deeply incorporated in its chiral cleft, (3) the existence of aqua ligands, (4) the irreversible formation of meso 2:1 complexes, and (5) the water-bridged heterochiral oligomerization of 1:1 complexes. We believe the present work has shown a new guiding principle for the structural design of chiral ligands and catalysts. Especially the importance of tridentate ligands, the trans-chelating structure, and the aqua complexes of transition metals should be emphasized. These new complexes may open a new entry to chiral protonic acid catalysts

Table 7. Solvent Effect and Use of Other Metal Complexes in Chiral Amplification[a]

			mol %							
				ligand						
entry	metal	ligand ee/%	metal	total	major[b]	minor[c]	time/h	endo:exo	yield/%	selectivity ee/%
1[d]	$Ni(ClO_4)_2 \cdot 6H_2O$	20	10	20	12	8	48	96:4	95	56
2[e]	$Ni(ClO_4)_2 \cdot 6H_2O$	20	10	20	12	8	48	97:3	quant	52
3[f]	$Ni(ClO_4)_2 \cdot 6H_2O$	20	10	20	12	8	48	96:4	62	19
4[g]	$Ni(ClO_4)_2 \cdot 6H_2O$	20	10	10	6	4	18	97:3	80	28
5	$Ni(SbF_6)_2 + 3H_2O$	20	10	20	12	8	12	97:3	quant	54
6	$Mg(ClO_4)_2$	20	10	10	6	4	48	86:14	98	20
7	$Mg(ClO_4)_2$	50	10	20	15	5	144	97:3	91	40
8	$FeCl_2 + 2AgClO_4 + 3H_2O$	20	10	10	6	4	96	98:2	quant	47
9	$CuCl_2 + 2AgClO_4 + 3H_2O$	20	10	10	6	4	96	97:3	96	87
10	$ZnI_2 + 2AgClO_4 + 3H_2O$	20	10	10	6	4	96	98:2	quant	94
11[h]	$Ni(ClO_4)_2 \cdot 6H_2O$	100	10	10	10	0	144	95:5	79	2
12[h]	$Ni(ClO_{42} \cdot 6H_2O$	20	10	10	6	4	144	97:3	84	0
13[h]	$NiBr_2 + 2AgClO_4$	100	10	10	10	0	48	87:13	95	38
14[h]	$NiBr_2 + 2AgClO_4$	20	10	20	12	8	48	99:1	99	23
15[h]	$NiBr_2 + 2AgClO_4 + 3H_2O$	100	10	10	10	0	96	93:7	79	12
16[h]	$NiBr_2 + 2AgClO_4 + 3H_2O$	20	10	10	6	4	48	87:13	94	13

[a] Unless otherwise referred, DBFOX/Ph ligand (*R,R*)-**1** was used. [b] Major enantiomer. [c] Minor enantiomer. [d] Solvent: 1,2-dichloroethane. [e] Solvent: $CH_2Cl_2-Et_2O$, 4:1 v/v. [f] Solvent: CH_2Cl_2−acetone, 4:1 v/v. [g] Additive; NH_2NH_2 (4 mol %). [h] Ligand: (*R,R*)-2,6-Pyridinediyl-2,2′-bis(4-phenyloxazoline) (pybox).

as well as base catalysts. Work along this line is now ongoing in our laboratory.

Experimental Section

General Procedure. Melting points were recorded on a JANACO MP Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO A-702 spectrometer. ^1H and ^{13}C NMR spectra were recorded with JEOL LA 600 (^1H NMR: 600 MHz) and LA 400 (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) instruments. Chemical shifts are reported in parts per million downfield (δ) from internal tetramethylsilane at 27 °C unless otherwise stated. Mass spectra were recorded with a JEOL-JMS-70 spectrometer operating at an ionization energy of 70 eV. Gas chromatography/mass spectra were recorded with Finnigan MAT GCQ apparatus. Elemental analyses were performed with a Hitachi 026 CHN analyzer. X-ray crystallography was made on an Enraf-Nonius FR590 computer-controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator. Data collection was performed with Cu Kα radiation (λ = 1.541 84 Å) with CAD-4 computer software (Enraf-Nonius, 1989).[53a] Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 16 reflections in the range $21° < \theta < 43°$, measured by the computer controlled diagonal slit method (CAD-4) of centering. Data reduction was made by a MolEN (Fair, 1990).[53b] The program used to solve the structure was a SIR92 system (Altomare et al., 1994),[53c] and that used to refine structure was SHELXL93 (Sheldrick, 1993).[53d] For preparative column chromatography, Wakogel C-200, Wako C-300, and Merck silica gel 60 were employed. High-performance liquid chromatography (HPLC) was measured on a TOSOH SC-8010 chromatograph attached to a Hibar LiChrosorb Si 60 column (Cica merck). Chiral HPLC analysis was performed on the same apparatus with a chiral column as described in the experimental procedures. Optical rotations were recorded with a Horiba SEPA-200 polarimeter. Flash chromatography was performed with an Eyera EF-10 apparatus on a 20 × 180 mm column packed with 0.04−0.063-mm silica gel 60. Micro vacuum distillation was performed with a Sibata GTO-250R Kugelrohr distilling apparatus.

Materials. 3-(2-Propenoyl)-2-oxazolidinone (7a): colorless solid; mp 80−81 °C; IR (KBr) 2950, 1760, 1660, 1600, 1400, 1200, 1120, 950, 800, 780, 690, and 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 4.0−4.2 (2H, m, H-4), 4.4−4.5 (2H, m, H-5), 5.91 (1H, dd, $J_{3'-2'}$ = 10.6 Hz and J_{gem} = 1.8 Hz, *cis*-H-3′), 6.56 (1H, dd, $J_{3'-2'}$ = 17.2 Hz and J_{gem} = 1.8 Hz, *trans*-H-3′), and 7.50 (1H, dd, $J_{2'-3'}$ = 17.2 Hz and 10.6 Hz, H-2′); ^{13}C NMR ($CDCl_3$) δ = 42.63 (C-4), 62.17 (C-5), 126.99 (C-2′), 131.82 (C-3′), 153.41 (C-2), and 165.08 (C-1′); MS (70 eV, relative intensity, %) *m*/*z* 142 (base peak, M^+), 141 (20), 121 (19), 120 (45), 100 (23), 93 (12), 92 (29), 91 (59), 88 (17), 77 (14), 67 (33), 66 (91), 65 (13), and 56 (47). Anal. Calcd for $C_6H_7NO_3$: C, 50.80; H, 4.73; N, 9.97. Found: C, 50.99; H, 4.88; N, 9.82.

3-((*E*)-2-Butenoyl)-2-oxazolidinone (7b): colorless viscous oil; IR (neat) 3600, 3000, 2950, 1780, 1690, 1620, 1490, 1450, 1380, 1220, 1130, 1100, 1050, 980, 920, 830, 760, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.96 (3H, d, $J_{4'-3'}$ = 5.1 Hz, H-4′), 4.0−4.2 (2H, m, H-4), 4.4−4.5 (2H, m, H-5), 7.18 (1H, dq, $J_{3'-2'}$ = 15.0 Hz and $J_{3'-4'}$ = 5.1 Hz, H-3′), and 7.50 (1H, d, $J_{2'-3'}$ = 15.0 Hz, H-2′); ^{13}C NMR ($CDCl_3$) δ = 18.50 (C-4′), 42.45 (C-4), 62.11 (C-5), 121.49 (C-2′), 146.73 (C-3′), 153.60 (C-2), and 165.18 (C-1′); MS (70 eV, relative intensity, %) *m*/*z* 155 (base peak, M^+), 154 (12), 128 (24), 127 (72), 126 (10), 89 (11), 88 (83), 87 (19), 86 (10), 77 (11), 71 (13), 70 (58), 67 (10), and 57 (13). Anal. Calcd for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.36; H, 5.78; N, 8.46.

3-((*E*)-2-Hexenoyl)-2-oxazolidinone (7c): colorless viscous oil; IR (neat) 2950, 1760, 1680, 1620, 1480, 1350, 1200, 1100, 1020, 970, 750, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.95 (3H, t, $J_{6'-5'}$ = 7.3 Hz, H-6′), 1.53 (2H, m, H-5′), 2.26 (2H, dt, $J_{4'-5'}$ = 7.5 Hz and $J_{4'-3'}$ = 5.9 Hz, H-4′), 4.0−4.2 (2H, m, H-4), 4.4−4.5 (2H, m, H-5), 7.19 (1H, dt, $J_{3'-2'}$ = 15.4 Hz and $J_{3'-4'}$ = 5.9 Hz, H-3′), and 7.36 (1H, d, $J_{2'-3'}$ = 15.4 Hz, H-2′); ^{13}C NMR ($CDCl_3$) δ = 13.69 (C-6′), 21.38 (C-5′), 34.67 (C-4′), 42.53 (C-4), 62.07 (C-5), 120.11 (C-2′), 151.56 (C-3′), 153.56 (C-2), and 165.35 (C-1′); MS (70 eV, relative intensity, %) *m*/*z* 183 (base peak, M^+), 168 (18), 142 (13), 141 (11), 140 (45), 124 (25), 98 (15), 97 (73), 96 (base peak), 95 (63), 88 (74), 84 (13), 83 (52), 82 (29), 81 (51), 80 (14), 71 (17), 70 (33), 69 (34), 68 (30), and 67 (17). Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 58.34; H, 6.90; N, 7.44.

3-((*E*)-2-Cinnamoyl)-2-oxazolidinone (7d): colorless solid; mp 151−152 °C; IR (KBr) 2950, 1750, 1670, 1600, 1490, 1350, 1200, 1100, 1030, 860, 750, 690, 590, and 490 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 4.0−4.2 (2H, m, H-4), 4.4−4.5 (2H, m, H-5), 7.3−7.5 (3H, m, Ph), 7.6−7.7 (2H, m, Ph), 7.84 (1H, d, $J_{2'-3'}$ = 15.8 Hz, H-2′), and 7.93 (1H, d, $J_{3'-2'}$ = 15.8 Hz, H-3′); ^{13}C NMR ($CDCl_3$) δ = 42.84 (C-4), 62.10 (C-5), 116.61, 128.78, 128.89, 130.69 (Ph), 134.54 (C-2′), 146.29 (C-3′), 153.63 (C-2), and 165.41 (C-1′); MS (70 eV, relative intensity, %) *m*/*z* 217 (base peak, M^+), 132 (51), 131 (23), 130 (31), 104 (26), 103 (base peak), 102 (46), and 77 (46). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.51; H, 5.15; N, 6.47.

4,6-Dibenzofurandicarboxylic Acid (3). To a THF solution of dibenzofuran (1 g, 5.95 mmol in 9 mL) was added dropwise, under dry nitrogen at −40 °C, butyllithium (1.6 M in hexane, 11.2 mL, 17.8 mmol) by use of a syringe. The mixture was stirred at 0 °C for 30 min and then at room temperature for 1 h, and finally it was heated under reflux for 3 h. After being cooled down to room temperature,

the mixture was poured onto dry ice. Water was added to dissolve the solid, and the aqueous solution was acidified with diluted hydrochloric acid to give a colorless precipitate. The solid was collected on a filter and washed with diethyl ether to give 4,6-dibenzofurandicarboxylic acid (3, 0.668 g, 44%): colorless solid; mp >300 °C; IR (KBr) 3400, 2800, 1700, 1490, 1290, 1190, 800, and 750 cm^{-1}; MS (70 eV, relative intensity, %) *m*/*z* 257 (14, $M^+ + 1$), 256 (23, M^+), 239 (23), 212 (17), 195 (51),194 (56), 140 (44), 140 (44), 139 (base peak), 138 (44), 137 (20), 127 (18), 111 (19), 97 (16), and 86 (12). This carboxylic acid **3** could not be purified by crystallization due to its low solubility in organic solvents. Therefore, it was used for the following transformation without further purification.

4,6-Dibenzofurandiyl-2,2′-bis[4(*R*)-phenyl-1,3-oxazoline] (*R*,*R*)-1). A mixture of 4,6-dibenzofurandicarboxylic acid (2 g, 7.81 mmol) and trifluoroacetic acid (10 mL) was stirred at room temperature for 30 min. To this mixture was added thionyl chloride (40 mL), and the mixture was heated under reflux for 13 h. The excess thionyl chloride was distilled out to give a residue, which was then dissolved in dry chloroform (40 mL). To this solution at 0 °C, was slowly added a chloroform solution (10 mL) of (*R*)-phenylglycinol (2.39 g, 17.2 mmol) and triethylamine (4.74 g, 46.8 mmol). After the mixture was stirred at room temperature for 24 h, additional thionyl chloride (16 mL) was added and the stirring was continued for 3 h. The resulting mixture was poured into ice water and extracted with chloroform (20 mL × 4). The combined extracts were washed with aqueous sodium carbonate and dried over sodium sulfate. The chloroform was evaporated in vacuo to give a solid residue, which was then treated with aqueous sodium hydroxide (2 g, 50 mmol in 24 mL of water) in a methanol (50 mL)−chloroform (24 mL) solution at room temperature for 24 h. The organic solvents were evaporated in vacuo at room temperature, and the residue was extracted with chloroform (20 mL × 3). The combined extracts were dried over sodium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with hexane−AcOEt, 1:1 v/v, to give colorless crystals of (*R*,*R*)-**1** (2.05 g, 63% for all steps). The enantiomeric purity of (*R*,*R*)-**1** was 98.3% ee by HPLC using a chiral column (Daicel Chiralcel OD-H with hexane−2-PrOH, 9:1 v/v, 1 mL/min, $t(R) = 23.7$ min, $t(S) = 27.4$ min): colorless solid (EtOAc−hexane); mp 134−135 °C; $[\alpha]^{25}_D$ 47.75 ($c = 1.07$, $CHCl_3$); IR (KBr) 3000, 1620, 1470, 1400, 1350, 1180, 1080, 640, 850, 750, 690, and 520 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 4.36$ (2H, t, $J_{gem} = J_{5-4} = 8.8$ Hz, one of H-5), 4.93 (2H, dd, $J_{5-4} = 10.3$ Hz and $J_{gem} = 8.8$ Hz, the other of H-5), 5.52 (2H, dd, $J_{4-5} = 10.3$ Hz and 8.8 Hz, H-4), 7.2−7.6 (10H, m, Ar), 7.44 (2H, t, $J = 7.7$ Hz, Ar), 8.11 (2H, dd, $J = 7.7$ and 1.5 Hz, Ar), and 8.19 (2H, dd, $J = 7.7$ and 1.5 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ = 69.95 (C-5 of oxazoline), 74.81 (C-4 of oxazoline), 113.24, 123.78, 124.85, 126.76, 127.47, 128.68, 128.74, 142.46, 154.37 (each Ar), and 162.30 (C-2 of oxazoline); MS (70 eV, relative intensity, %) *m*/*z* 459 (37), 458 (52, M^+), 457 (14), 428 (12), 328 (24), 327 (40), 309 (40), 308 (75), 307 (17), 282 (11), 281 (23), 280 (18), 220 (18), 164 (21), 91 (72), 90 (85), and 89 (base peak). Anal. Found: C, 78.31; H, 4.84; N, 6.20%. Calcd for $C_{30}H_{22}N_2O_3$: C, 78.59; H, 4.84; N, 6.11.

Single crystals of (*R*,*R*)-**1** were grown from ethyl acetate−hexane and were monoclinic having space group $P2_12_12_1$, $a = 19.326(2)$ Å, $b = 22.874(10)$ Å, $c = 5.287(10)$ Å, $V = 2337.2(45)$ Å^3, $Z = 4$. The final *R* factor was 0.0811 for 6659 measured reflections.[25]

4-[*N*-(2-Iodo-1(*R*)-phenylethyl)carbamoyl]-6-(4(*R*)-phenyl-2-oxazolinyl)dibenzofuran (10). Magnesium turnings and 2 equiv of iodine were treated with (*R*,*R*)-**1** in dichloromethane at room temperature overnight. By continuous stirring, a red solid of **10** precipitated from the resulting colorless solution: ^{1}H NMR ($CDCl_3$) $\delta = 3.35$ (1H, dd, $J_{gem} = 10.3$ Hz and $J_{CH_2-CH} = 5.1$ Hz, one of CH_2I), 3.35 (1H, t, $J_{gem} = 10.3$, Hz the other of CH_2I), 4.27 (1H, t, $J_{gem} = J_{5-4} = 8.4$ Hz, one of H-5), 4.79 (1H, t, $J_{5-4} = J_{gem} = 8.4$ Hz, the other of H-5), 5.40 (1H, dd, $J_{CH-CH_2} = 10.3$ and 5.1 Hz, CH(Ph)CH_2I), 5.55 (1H, t, $J_{4-5} = 8.4$ Hz, H-4), 7.1−7.6 (10H, m, Ar), 7.47 (1H, t, $J = 7.7$ Hz, Ar), 7.50 (1H, t, $J = 7.7$ Hz, Ar), 8.09 (1H, d, $J = 7.7$ Hz, Ar), 8.13 (1H, d, $J = 7.7$ Hz, Ar), 8.27 (1H, d, $J = 7.7$ Hz, Ar), and 8.82 (1H, d, $J = 7.7$ Hz, Ar); MS (70 eV, relative intensity, %) *m*/*z* 459 (27), 458 (35, M^+), 328 (30), 327 (51), 309 (57), 308 (90), 282 (14), 281 (29), 220 (17), 208 (34), 207 (61), 165 (11), 164 (31), 128 (base peak), 127 (63), 103 (12), 91 (44), 90 (69), and 89 (92). Anal. Found: C, 61.44; H, 3.95; N, 4.78%. Calcd for $C_{30}H_{23}N_2O_3I$: C, 61.04; H, 4.35; N, 4.68.

General Procedure for the Diels−Alder Reactions Catalyzed by the DBFOX/Ph Complexes Prepared from Nickel(II) Perchlorate Hexahydrate. The reaction of cyclopentadiene with 3-acryloyl-2-oxazolidinone is described as a typical example: A mixture of (*R*,*R*)-**1** (DBFOX/Ph, 32.5 mg, 0.071 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (25.9 mg, 0.071 mmol) in dichloromethane (4.4 mL) was stirred at room temperature for 3 h, during which time most of the nickel salt was dissolved. At −40 °C, 3-acryloyl-2-oxazolidinone (**7a**, 0.1 g, 0.71 mmol) and the freshly distilled cyclopentadiene (0.468 g, 0.571 mL, 7.09 mmol) were added in this order. The reaction was performed at −40 °C and monitored by TLC. After the completion of reaction, saturated aqueous ammonium chloride was added and the mixture was extracted with dichloromethane (10 mL × 3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with hexane−AcOEt, 3:1 v/v, to give a mixture of endo and exo isomers of cycloadduct **8a** (0.147 g, 100%). The endo:exo ratio was evaluated on the basis of the ^{1}H NMR spectrum and the enantiomeric purity by HPLC (Daicel Chiralcel OD, hexane−*i*-PrOH, 99/1 v/v, flow rate = 1 L/min, $t(R) = 69.9$ min, $t(S) = 58.9$ min).

The aqua complexes of DBFOX/Ph and magnesium, cobalt(II), manganese(II), zinc, and copper(II) perchlorates can be prepared according to the equiv procedures. The aqua complex between DBFOX/Ph and iron(II) was prepared by adding 3 equiv of water to the corresponding anhydrous complex (see the procedure for the anhydrous nickel(II) complex). Results of Diels−Alder reactions in the presence of these catalysts are summarized in Tables 1 and 4.

(1*S*,2*S*,4*S*)-3-(Bicyclo[2.2.1]hept-5-en-2-ylcarbonyl)-2-oxazolidinone (8a): colorless solid; mp 86−87 °C; $[\alpha]^{25}_D$−148.82 (98% ee estimated on the basis of HPLC using a chiral column (Daicel Chiralcel OD with hexane−2-PrOH, 99:1 v/v), $c = 1.02$, $CHCl_3$); IR (KBr) 2950, 1760, 1490, 1350, 1100, 1030, 750, and 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.3−1.7 (3H, m, H-3 and one of H-7), 1.9−2.1 (1H, m, the other of H-7), 2.94 (1H, m, H-1 or H-4), 3.31 (1H, m, H-4 or H-1), 3.8−4.1 (3H, m, H-2 and H-4′), 4.40 (2H, t, $J_{gem} = J_{5'-4'} = 8.1$ Hz, H-5′), 5.88 (1H, dd, $J_{5-6} = 5.5$ and $J_{5-4} = 2.9$ Hz, H-5), and 6.25 (1H, dd, $J_{6-5} = 5.5$ and $J_{6-1} = 2.9$ Hz, H-6); ^{13}C NMR ($CDCl_3$) $\delta = 29.56$ (C-3), 42.89, 42.95, 43.21, 46.39 (C-1, C-2, C-4, and C-4′), 50.18 (C-7), 61.97 (C-5′), 131.63, 138.11 (C-5 and C-6), 153.41 (C-2′), and 174.75 (CO); MS (70 eV, relative intensity, %) *m*/*z* 207 (11, M^+), 143 (39), 142 (base peak), 141 (31), 121 (25), 120 (61), 100 (33), 93 (16), 92 (40), 91 (78), and 88 (24). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.64; H, 6.17; N, 6.76.

(1*S*,2*S*,3*R*,4*R*)-3-(3-Methylbicyclo[2.2.1]hept-5-en-2-ylcarbonyl)-2-oxazolidinone (8b): colorless solid; mp 93−94 °C; $[\alpha]^{25}_D$ −158.59 (93% ee estimated on the basis of HPLC using a chiral column (Daicel Chiralcel OD with hexane−2-PrOH, 50:1 v/v), $c = 1.00$, CCl_4); IR (KBr) 3200, 1780, 1700, 1490, 1400, 1400, 1220, 1100, 1050, 770, 730, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 1.13$ (3H, d, $J_{Me-3} = 7.0$ Hz, Me), 1.46 (1H, d, $J_{gem} = 8.8$ Hz, one of H-7), 1.71 (1H, d, $J_{gem} = 8.8$ Hz, the other of H-7), 2.10 (1H, m, H-3), 2.53 (1H, br s, H-4), 3.28 (1H, br s, H-1), 3.54 (1H, dd, $J = 4.4$ and 3.7 Hz, H-2), 3.8−4.1 (2H, m, H-4′), 4.40 (2H, t, $J_{gem} = J_{5'-4'} = 8.1$ Hz, H-5′), 5.79 (1H, dd, $J_{5-6} = 5.5$ Hz and $J_{5-4} = 2.9$ Hz, H-5), and 6.38 (1H, dd, $J_{6-5} = 5.5$ Hz and $J_{6-1} = 2.9$ Hz, H-6); ^{13}C NMR ($CDCl_3$) $\delta = 20.43$ (3-Me), 36.50 (C-3), 43.04, 47.16, 47.49, 49.55 (C-1, C-2, C-4, and C-4′), 51.32 (C-7), 61.90 (C-5′), 130.97, 139.72 (C-5 and C-6), 153.49 (C-2′), and 174.45 (CO); MS (70 eV, relative intensity, %) *m*/*z* 222 (17), 221 (35, M^+), 158 (19), 157 (73), 155 (base peak), 135 (40), 134 (73), 133 (21), 119 (30), 115 (48), 114 (60), 113 (26), 107 (11), 106 (38), 105 (45), 104 (13), 103 (15), 92 (33), 91 (59), and 88 (95). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 64.86; H, 6.47; N, 6.30.

(1*S*,2*S*,3*R*,4*R*)-3-(3-Propylbicyclo[2.2.1]hept-5-en-2-ylcarbonyl)-2-oxazolidinone (8c): colorless oil; $[\alpha]^{25}_D$ −158.85 (94% estimated on the basis of HPLC using a chiral column (Daicel Chiralcel OD with hexane−2-PrOH, 50:1 v/v), $c = 0.37$, CCl_4); IR (KBr) 3200, 1780, 1700, 1490, 1400, 1220, 1100, 1050, 770, 730, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.86$ (3H, t, $J = 7.3$ Hz, Me), 1.0−1.5 (4H, m, *n*-Pr),

1.67 (1H, m, one of H-7), 1,99 (1H, m, the other of H-7), 2.63 (1H, br s, H-4), 3.26 (1H, br s, H-1), 3.59 (1H, t, $J = 4.0$, H-2), 3.8−4.1 (2H, m, H-4′), 4.41 (2H, t, $J_{gem} = J_{5'-4'} = 8.1$ Hz, H-5′), 5.78 (1H, dd, $J_{5-6} = 5.5$ Hz and $J_{5-4} = 2.6$ Hz, H-5), and 6.36 (1H, dd, $J_{6-5} = 5.5$ Hz and $J_{6-1} = 3.3$ Hz, H-6); ^{13}C NMR ($CDCl_3$) $\delta = 14.25$ (Me of *n*-Pr), 22.02 (C-2 of *n*-Pr), 37.84 (C-7), 42,46, 43.04, 47.13, 47.60, 47.66 (C-1, C-2, C-3, C-4, and C-3 of *n*-Pr), 49.99 (C-7), 61.88 (C-5′), 131.09, 139.71 (C-5 and C-6), 153.50 (C-2′), and 174.55 (CON); MS (70 eV, relative intensity, %) *m*/*z* 250 (21), 249 (28, M^+), 186 (46), 164 (34), 163 (base peak), 162 (97), 161 (14), 148 (17), 147 (12), 144 (17), 141 (28), 135 (20), 134 (67), 133 (42), 130 (12), 129 (12), 121 (15), 120 (82), 119 (83), 118 (27), 107 (27), 106 (64), 104 (42), 103 (37), 99 (10), 95 (32), 93 (29), 92 (70), 90 (24), 89 (55), 87 (15), 81 (25), 80 (21), 79 (48), 78 (35), and 77 (56). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.13; H, 7.63; N, 5.40.

(1*S*,2*R*,3*R*,4*R*)-3-(3-Phenylbicyclo[2.2.1]hept-5-en-2-ylcarbonyl)-2-oxazolidinone (8d); colorless solid; $[\alpha]^{25}_D$ −45.23 (51% ee estimated on the basis of HPLC using a chiral column (Daicel Chiralcel AD with hexane−2-PrOH, 19:1 v/v), $c = 0.37$, CCl_4); IR (KBr) 3000, 1780, 1690, 1490, 1400, 1220, 1110, 1030, 730, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 1.2-2.0$ (2H, m, H-7), 3.00, 3.34, 3.47 (each 1H, m, H-1, H-3, and H-4, 3.9−4.3 (3H, m, H-2 and H-4′), 4.3−4.5 (2H, H-5′), 5.93 (1H, dd, $J = 5.5$ and 2.9 Hz, H-5 or H-6), and 6.53 (1H, dd, $J = 5.5$ and 2.9 Hz, H-6 or H-5), and 7.1−7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) $\delta = 43.02$, 46.94, 47.50, 48.16, 49.75 (C-1, C-2, C-3, C-4, and C-4′), 50.31 (C-7), 61.94 (C-5′), 126.16, 127.63, 128.02, 128.51 (Ar), 132.18, 140.23 (C-5 and C-6), 153.40 (C-2′), and 173.85 (CO); MS (70 eV) (relative intensity, %) *m*/*z* 283 (12, M^+), 221 (16), 220 (11), 216 (40), 198 (10), 197 (62), 196 (65), 195 (20), 189 (14), 177 (62), 176 (73), 174 (20), 173 (30), 172 (20), 169 (36), 164 (19), 155 (14), 154 (35), 151 (12), 147 (20), 146 (27), 142 (18), 141 (19), 140 (17), 134 (12), and 84 (10). Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 70.60; H, 6.05; N, 4.48.

(1*S*,2*S*,4*S*)-1-(Bicyclo[2.2.1]hept-5-en-2-ylcarbonyl)-2-pyrrolidinone (14): colorless solid; mp 86−89 °C; $[\alpha]^{25}_D$ −170.83 (98% ee estimated on the basis of HPLC using a chiral column (Daicel Chiralcel OD with hexane−2-PrOH, 99:1 v/v), $c = 1.57$, $CHCl_3$); IR (KBr) 2900, 1900, 1510, 1200, 1150, 920, 850, 720, 650, and 590 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 1.3-1.6$ (3H, m, H-7 and one of H-3), 1.92 (1H, ddd, $J_{3-2} = 8.0$ Hz, $J_{3-4} = 3.6$ Hz, and $J_{gem} = 11.0$ Hz, the other of H-3), 1.9−2.2 (2H, m, H-4′), 2.62 (2H, t, $J_{4'-3'} = 8.0$ Hz, H-3′), 2.92 (1H, m, H-4), 3.26 (1H, m, H-1), 3.6−3.9 (2H, m, H-2 and one of H-5′), 3.98 (1H, ddd, $J_{gem} = 8.9$ Hz and $J_{5'-4'} = 4.4$ and 3.6 Hz, the other of H-5′), 5.85 (1H, dd, $J_{5-6} = 5.5$ and $J_{5-4} = 2.9$ Hz, H-5) and 6.25 (1H, dd, $J_{6-5} = 5.5$ Hz and $J_{6-1} = 2.9$ Hz, H-6); ^{13}C NMR ($CDCl_3$) $\delta = 17.23$ (C-4′), 29.56 (C-3), 34.03, 42.88, 44.64, 45.67, 46.11 (C-1, C-2, C-4, C-3′, and C-5′), 50.09 (C-7), 131.83, 137.88 (C-5 and C-6), 175.02, and 175.61 (C-2′ and CO); MS (70 eV, relative intensity, %) *m*/*z* 205 (21, M^+), 140 (68), 139 (26), 120 (base peak), 111 (14), 99 (13), 98 (29), 92 (19), 91 (40), and 86 (54). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 69.26; H, 7.26; N, 6.55.

Methyl (1*S*,2*R*,3*R*,4*R*)-3-Phenylbicyclo[2.2.1]hept-5-en-2-ylglyoxylate (16): colorless oil; $[\alpha]^{25}_D$ −111.35 (68% ee estimated on the basis of HPLC using a chiral column (Daicel Chiralcel AD with hexane−2-PrOH, 50:1 v/v), $c = 1.57$, $CHCl_3$); IR (KBr) 3000, 1720, 1600, 1440, 1240, 1080, 1320, 900, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 1.63$ (1H, dd, $J_{gem} = 8.7$ Hz and $J = 1.7$ Hz, H-7), 1.93 (1H, d, $J_{gem} = 8.7$ Hz, the other of H-7), 3.05 (1H, m, H-4), 3.24 (1H, d, $J_{3-2} = 4.9$ Hz, H-3), 3.48 (1H, m, H-1), 3.73 (1H, dd, $J_{2-3} = 4.9$ Hz and $J_{2-1} = 3.4$ Hz, H-2), 3.84 (3H, s, COOMe), 5.94 (1H, dd, $J_{6-5} = 5.5$ Hz and $J_{6-1} = 2.7$ Hz, H-6), 6.44 (1H, dd, $J_{5-6} = 5.5$ Hz and $J_{5-4} = 3.1$ Hz, H-5), and 7.4−7.1 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) $\delta = 45.56$, 47.20, 47.73, 49.10, 52.82, 56.69 (Me, C-1, C-2, C-3, C-4, and C-7), 126.25, 127.43, 128.57, 132.70 (each Ph), 139.91, 143.41 (C-5 and C-6), 162.27 (COCOOMe), and 194.12 (COCOOMe); MS (70 eV, relative intensity, %) *m*/*z* 256 (0.23, M^+), 191 (66), 131 (base peak), 103 (23), 77 (10), and 66 (17). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 72.70; H, 6.18.

3-(1-Methylcyclohexen-4-ylcarbonyl)-2-oxazolidinone (17): colorless solid; mp 51−53 °C; $[\alpha]^{25}_D$ −71.29 (56% ee estimated on the basis of HPLC using a chiral column (Daicel Chiralcel ODH with hexane−2-PrOH, 9:1 v/v), $c = 1.00$, $CHCl_3$); IR (KBr) 3000, 2900, 1760, 1680, 1320, 1200, 1110, 1040, 910, 850, 800, 750, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 1.66$ (3H, s, Me), 1.5−2.2 (6H, m, H-3, H-5, and H-6), 3.66 (1H, m, H-4), 4.02 (2H, t, $J_{4'-5'} = 8.0$ Hz, H-4′), 4.41 (2H, t, $J_{5'-4'} = 8.0$ Hz, H-5′), and 5.39 (1H, m, H-2); ^{13}C NMR ($CDCl_3$) $\delta = 23.42$ (Me), 25.94, 27.47, 29.52 (C-3, C-5, and C-6), 38.20 (C-4), 42.84 (C-4′), 61.94 (C-5′), 119.09 (C-2), 133.73 (C-1), 153.21 (C-2′), and 176.72 (CO); MS (70 eV, relative intensity, %) *m*/*z* 209 (66, M^+), 122 (81), 107 (26), 95 (12), 94 (43), 91 (13), 88 (32), 79 (base peak), 77 (19), and 67 (17). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 62.75; H, 7.13; N, 6.62.

(2*S*)-2-Bromobicyclo[2.2.1]hept-5-ene-2-carboxaldehyde (19). Product **19** was characterized by comparison of the spectral data with those of the authentic sample.[51] Its enantioselectivity (86% ee) was based on the ^{1}H NMR spectral analysis using a chiral shift reagent, europium-(III) (−)-tris[3-(heptafluoropropylhydroxymethylene)camphorate (Eu-(hfc)$_3$).[52]

Preparation of the Anhydrous DBFOX/Ph Nickel Complex. A mixture of (*R*,*R*)-**1** (32.5 mg, 0.071 mmol), anhydrous $NiBr_2$ (15.5 mg, 0.071 mmol), and anhydrous $AgClO_4$ (29.4 mg, 0.142 mmol) in dry dichloromethane (4.4 mL) was stirred under dry nitrogen at room temperature for 6 h, during which time a gray precipitate of silver bromide appeared. The resulting suspension was used without filtration for the Diels−Alder reactions as follows: At −40 °C, 3-acryloyl-2-oxazolidinone (0.1 g, 0.71 mmol) and freshly distilled cyclopentadiene (0.468 g, 0.571 mL, 7.09 mmol) were added to this suspension. The reaction was performed at the same temperature (monitored by TLC). After the completion of reaction, similar quenching and purification procedures were applied.

Other anhydrous DBFOX/Ph complexes were prepared according to a similar procedure by using anhydrous metal halides such as $MnBr_2$, $FeCl_2$, $CoBr_2$, $CuCl_2$, and ZnI_2. The DBFOX/Ph complexes bearing counteranions other than perchlorate were prepared in one of the following ways: (1) treatment of (*R*,*R*)-**1** with $MgBr_2$, MgI_2, $Mg(OTf)_2$, or $Cu(OTf)_2$; (2) treatment of (*R*,*R*)-**1** with $MgBr_2$, MgI_2, or $FeCl_2$, followed by treatment with I_2; or (3) treatment of the anhydrous nickel-(II) or copper(II) complex with $AgSbF_6$.

Preparation of the 1:1 Hydroxo Complex [*R*-DBFOX/Ph·NiClO$_4$-(OH)·2H$_2$O] (A). Ligand (*R*,*R*)-**1** (65 mg, 0.142 mmol) and Ni-$(ClO_4)_2$·6H$_2$O (52 mg, 0.142 mmol) were stirred in dichloromethane (4 mL) at room temperature for 5 h, during which time the insoluble nickel salt became dissolved and then a pale blue solid started to precipitate. The precipitate was filtered off, and the filtrate was evaporated in vacuo. The residue was washed with dichloromethane and dried in a vacuum at room temperature for 3 days to give a pale blue solid (95 mg, 100%): mp >300 °C; FAB-MS (matrix: *m*-nitrobenzyl alcohol) (relative intensity, %) *m*/*z* 619 (15), 618 (18), 617 (51, DBFOX/Ph + $NiClO_4$), 616 (24), 615 (65), 518 (17), 517 (17), and 516 (39). Anal. Found: C, 53.15; H, 4.25; N, 4.27%. Calcd for $C_{30}H_{27}N_2O_{10}ClNi$: C, 53.77; H, 4.06; N, 4.18.

Preparation of the 1:1 Aqua Complex [*R*-DBFOX/Ph·Ni(ClO$_4$)$_2$·3H$_2$O] (*R*,*R*)-9). A mixture of (*R*,*R*)-**1** (32.5 mg, 0.071 mmol), $NiBr_2$ (15.5 mg, 0.071 mmol), and $AgClO_4$ (29.4 mg, 0.142 mmol) in dry dichloromethane (4 mL) was stirred overnight under dry nitrogen at room temperature. Filtration to remove the silver salt that precipitated gave a filtrate, which was treated in one of the following manners: (1) To the filtrate was added benzene, and this solution was allowed to stand at room temperature to give cubic crystals of the above complex (82 mg, 71%). (2) The dichloromethane was evaporated in vacuo, the residue was dissolved in acetone, dichloromethane was added, and finally the solution was allowed to stand at room temperature to give prism crystals of the above complex. (3) To the dichloromethane filtrate

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was added 3-acetyl-2-oxazolidinone (9 mg, 0.071 mmol), and the resulting solution was allowed to stand at room temperature to give prism crystals of the above complex: mp >300 °C; FAB-MS (matrix: *m*-nitrobenzyl alcohol) (relative intensity, %) *m*/*z* 619 (23), 618 (27), 617 (77, DBFOX/Ph + $NiClO_4$), 616 (36), 615 (base peak), 518 (24), 517 (23), 516 (53), and 515 (13). Anal. Found: C, 46.50; H, 3.79; N, 3.69%. Calcd for $C_{30}H_{28}N_2O_{14}Cl_2Ni$: C, 46.79; H, 3.66; N, 3.64.

A single crystal of (*R*,*R*)-**9** was orthorhombic, having space group $P2_12_12_1$, a = 18.008(4) Å, b = 0.058(3) Å, c = 9.3410(10) Å, V = 3374.0(10) Å^3, Z = 4. The final *R* factor was 0.0597 for 3866 measured reflections.[25]

Preparation of the Meso 2:1 Complex [(*R*-DBFOX/Ph)$_2$Ni] (*meso*-22). This 2:1 complex was obtained by either of the following preparation methods: (1) Ligand (*R*,*R*)-**1** (62.7 mg, 0.137 mmol), (*S*,*S*)-**1** (62.7 mg, 0.137 mmol), and $Ni(ClO_4)_2 \cdot 6H_2O$ (50 mg, 0.137 mmol) were stirred in dichloromethane (4 mL) at room temperature for 3 h. The pale blue precipitate was collected on a filter, washed with dichloromethane, and dried in vacuo for 4 days to give the 2:1 complex *meso*-**22** (102 mg, 63%). (2) Ligand (*R*,*R*)-**1** (32.5 mg, 0.071 mmol) was treated with $Ni(ClO_4)_2 \cdot 6H_2O$ (26 mg, 0.071 mmol) in dichloromethane (4 mL) at room temperature for 3 h, during which time some precipitate appeared. Acetone (2 mL) was added to dissolve the precipitate. To this solution was added dropwise a solution of (*S*,*S*)-**1** (32.5 mg, 0.071 mmol) in dichloromethane (1 mL), and the resulting solution was allowed to stand at room temperature. The pale blue precipitate was collected on a filter and washed with dichloromethane to give the 2:1 complex *meso*-**22** (41 mg, 48%): mp >300 °C; FAB-MS (matrix: *m*-nitrobenzyl alcohol) (relative intensity, %) *m*/*z* 1075 (11, 2DBFOX/Ph + $NiClO_4$), 1073 (11), 619 (12), 618 (14), 617 (40, DBFOX/Ph + $NiClO_4$), 616 (18), 615 (53), 519 (17), 518 (45), 517 (40), 516 (base peak), and 515 (10). Anal. Found: C, 60.33; H, 4.09; N, 4.59%. Calcd for $C_{60}H_{46}N_4O_{15}Cl_2Ni$: C, 60.43; H, 3.89; N, 4.90.

A single crystal of *meso*-**22** was orthorhombic having space group *Pbca*, a = 22.606(2) Å, b = 21.275(5) Å, c = 24.126(2) Å, V = 11603.2(31) Å^3, Z = 8. The data collection was carried out at 200 K by use of a nitrogen-stream cryostat system, and the final *R* factor was 0.1004 for 11 809 measured reflections.[25] The analysis was not completed because of the disorder of the acetone and the perchlorate ions. To solve this problemrequires a spherical crystal and correction of absorption.

Preparation of Single Crystals of Heterochiral Oligomers of 1:1 Aqua Complex DBFOX/Ph·Ni(ClO$_4$)$_2$·3H$_2$O (D). Equimolar amounts (23 mg, 0.03 mmol each) of the pure enantiomers of aqua complexes (*R*,*R*)-**9** and (*S*,*S*)-**9** were mixed together with 3-acetyl-2-oxazolidinone (3.9 mg, 0.03 mmol) in dichloromethane (4 mL). Stirring this mixture at room temperature for 2 h resulted in a clear solution. This solution was allowed to stand at room temperature for a few days to give single crystals of the heterochiral oligomers of 1:1 aqua complex DBFOX/Ph·$Ni(ClO_4)_2 \cdot 3H_2O$ (**D**, 27 mg, 17%).

A single crystal of **D** was triclinic having a space group $P\bar{1}$, a = 12.944(2) Å, b = 13.855(2) Å, c = 12.721(2) Å, α = 106.020(10)°, β = 114.950(10)°, γ = 64.420(10)° V = 1953/4(5) Å^3, Z = 2. The final *R* factor was 0.0743 for 7879 measured reflections.[25]

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