

Metal complexes of chiral binaphthyl Schiff-base ligands and their application in stereoselective organic transformations

Chi-Ming Che*, Jie-Sheng Huang

Department of Chemistry and Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong, Pokfulam Road, Hong Kong, Hong Kong

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Abstract

Condensations of aromatic aldehydes with 2,2'-diamino-1,1'-binaphthyl or 2-amino-2'-hydroxy-1,1'-binaphthyl afford various chiral binaphthyl Schiff-base ligands, the most common of which are potentially tetradentate with a N₂O₂ donor set. The chiral binaphthyl Schiff-base ligands have been shown to form stable complexes with metal ions of Al(III), Ti(IV), Cr(III), Mn(II)/Mn(III), Fe(II)/Fe(III), Co(II)/Co(III), Ni(II), Cu(II), Zn(II), Y(III), Zr(IV), Ru(II), and Pd(II); some of such complexes have been characterized by X-ray crystallography. Catalytic studies reveal that these types of chiral metal complexes are active catalysts for stereoselective organic transformations including hydroxylation of styrene, aldol reactions, alkene epoxidation, trimethylsilylcyanation of aldehydes, desymmetrization of *meso*-*N*-sulfonylaziridine, Baeyer-Villiger oxidation of aryl cyclobutanone, Diels-Alder reactions of 1,2-dihydropyridine, and ring-opening polymerization of lactide.

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1. Introduction

The design and synthesis of chiral ligands that, upon coordination with metal ions, can induce high stereoselectivity for organic transformations constitute an important issue in modern coordination chemistry. In

* Corresponding author. Tel.: +852-2859-2154; fax: +852-2857-1586.

E-mail address: cmche@hku.hk (C.-M. Che).

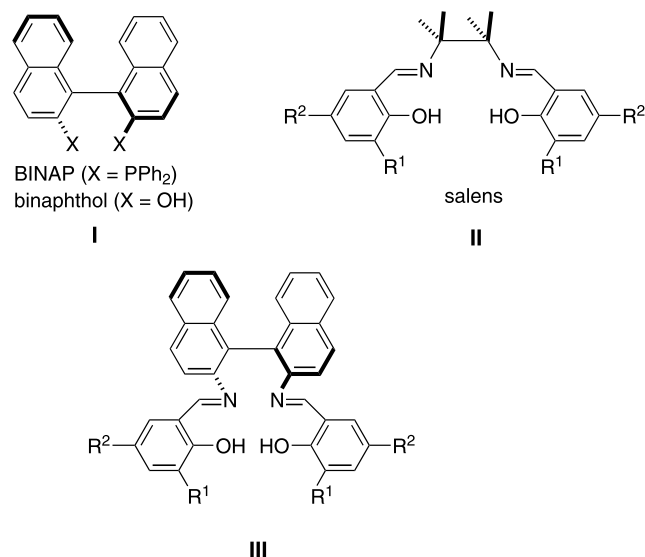


Fig. 1. Schematic structure of chiral C_2 -symmetric binaphthyl ligands **I**, Schiff-base ligands **II**, and binaphthyl Schiff-base ligands **III**.

this context, a lot of attention has been directed to C_2 -symmetric binaphthyl ligands such as BINAP and binaphthol (**I**, Fig. 1) [1,2] and chiral Schiff-base ligands such as salens (**II**, Fig. 1) [3–6]. Recently, there has been increasing interest in utilizing a ‘hybridized’ form of binaphthyl ligands and salens, i.e. binaphthyl Schiff-base ligand **III** [7–27] shown in Fig. 1, as a chiral auxiliary for metal-mediated stereoselective catalytic processes.

Chiral binaphthyl Schiff-base ligand **III** can be traced back to 1968. In that year Holm and co-workers reported the preparation of the first example of **III**, which bears substituents of $R^1 = ^s\text{Bu}$ and $R^2 = \text{Me}$ [28]. Since then, a wide variety of binaphthyl Schiff-base ligands **III** have been prepared, as shown in Fig. 2. The syntheses and structures of metal complexes of these chiral ligands and the catalytic properties of such metal complexes toward various organic transformations are the main concern of this review.

Note that there are other types of chiral binaphthyl Schiff-base ligands known in the literature, such as **IV** [29] and **V** [30–35] shown in Fig. 3. A partially hydrogenated form of **III** (i.e. **VI** in Fig. 3) [13,16] and the ligand **VII** [36] shown in Fig. 3 have also been reported. Because of the close relationship of these ligands with **III**, their metal complexes are also included here.

Tetradentate Schiff-base ligands containing a biphenyl (or its derivatives) rather than binaphthyl bridge constitute another important type of the analogues of **III**. The metal complexes with such ligands and their catalytic properties are described in the review by Scott and Knight in this issue of Coord. Chem. Rev. [37].

Fig. 2 shows the general structure of chiral binaphthyl Schiff-base ligands **III** and a table of specific examples. The structure is identical to **III** in Fig. 1. The table lists 33 examples (H₂L¹ to H₂L³³) with their substituents R¹ and R².

	R ¹	R ²		R ¹	R ²
H ₂ L ¹	H	H	H ₂ L ¹⁹	Me	Cl
H ₂ L ²	F	F	H ₂ L ²⁰	Et	Cl
H ₂ L ³	Cl	Cl	H ₂ L ²¹	Bu ^t	Cl
H ₂ L ⁴	Br	Br	H ₂ L ²²	Bu ^s	Me
H ₂ L ⁵	I	I	H ₂ L ²³	Bu ^t	Me
H ₂ L ⁶	Bu ^t	Bu ^t	H ₂ L ²⁴	Ad	Me
H ₂ L ⁷	NO ₂	NO ₂	H ₂ L ²⁵	Cl	Bu ^t
H ₂ L ⁸	H	Bu ^t	H ₂ L ²⁶	SP ⁱ	Bu ^t
H ₂ L ⁹	H	Ph	H ₂ L ²⁷	SPh	Bu ^t
H ₂ L ¹⁰	H	Cl	H ₂ L ²⁸	Bu ^t	OMe
H ₂ L ¹¹	H	NO ₂	H ₂ L ²⁹	Me	NO ₂
H ₂ L ¹²	Me	H	H ₂ L ³⁰	Et	NO ₂
H ₂ L ¹³	Et	H	H ₂ L ³¹	Pr ⁱ	NO ₂
H ₂ L ¹⁴	Bu ^t	H	H ₂ L ³²	Bu ^t	NO ₂
H ₂ L ¹⁵	OMe	H	H ₂ L ³³	Cl	NO ₂
H ₂ L ¹⁶	OEt	H			
H ₂ L ¹⁷	SPh	H			
H ₂ L ¹⁸	Cl	H			

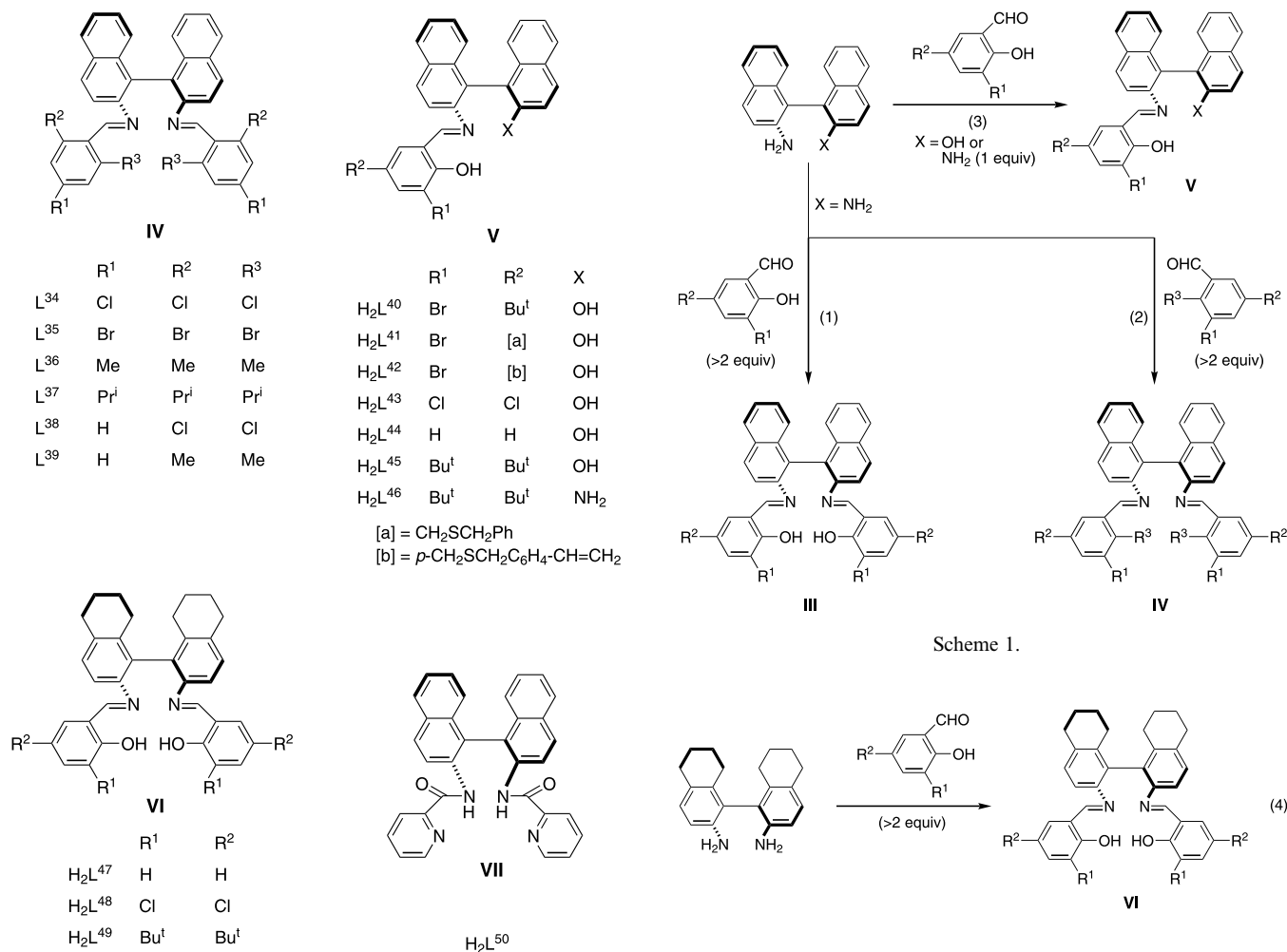
Ad = adamantyl

Fig. 2. Chiral binaphthyl Schiff-base ligands **III** reported in the literature.

2. Synthesis and structure of chiral binaphthyl Schiff-base ligands

Chiral binaphthyl Schiff-base ligands **III** (H₂L^{1–33}, Fig. 2) can be generally prepared by condensation of enantiomerically pure 2,2'-diamino-1,1'-binaphthyl and ≥ 2 equivalents of the respective salicylaldehyde derivative, as demonstrated by the groups of Holm [28], Sakiyama, Okawa [38], Meunier [8,9], Che [10,13,24], Stack [11], and Rawal [27] (reaction (1) in Scheme 1). From similar reactions (reaction (2) in Scheme 1), Suga, Ibata and co-worker [29] prepared type-IV ligands L^{34–39} (Fig. 3).

In 1994, Carreira and co-workers reported the first example of chiral binaphthyl Schiff-base ligands **V** (H₂L⁴⁰ in Fig. 3), which was prepared from condensation of 3-bromo-5-*tert*-butyl-salicylaldehyde and enantiomerically pure 2-amino-2'-hydroxy-1,1'-binaphthyl (reaction (3) in Scheme 1) [30]. Similar reactions of other salicylaldehydes with enantiomerically pure 2-amino-2'-hydroxy-1,1'-binaphthyl afforded chiral type-V ligands H₂L^{41–43}, as described by Salvadori [34], Che



Scheme 1.

Scheme 2.

Fig. 3. Schematic structure of binaphthyl Schiff-base ligands **IV** and **V** and their analogues **VI** and **VII**.

[13] and co-workers. Cai and co-workers prepared *rac*-H₂L^{44,45} from reaction of respective salicylaldehydes with crude 2-amino-2'-hydroxy-1,1'-binaphthyl [39]. By treating enantiomerically pure 2,2'-diamino-1,1'-binaphthyl with ca. 1 equivalent of 3,5-di-*tert*-butylsalicylaldehyde (reaction (3) in Scheme 1), Che and co-workers obtained the chiral ligand H₂L⁴⁶ (Fig. 3) [13].

Che and co-workers also prepared ligands **VI** (H₂L^{47–49}, Fig. 3) from the same reaction as for **III** except that enantiomerically pure 5,5',6,6',7,7',8,8'-octahydro-2,2'-diamino-1,1'-binaphthyl was used instead of 2,2'-diamino-1,1'-binaphthyl (reaction (4) in Scheme 2) [13,16]. By treating enantiomerically pure 2,2'-diamino-1,1'-binaphthyl with pyridine-2-carbonyl chloride (reaction (5) in Scheme 2), these workers obtained the chiral type-**VII** ligand H₂L⁵⁰ (Fig. 3) [36].

Of the 50 reported examples of ligands **III–VII**, only four have been characterized by X-ray structure determination. The first X-ray crystal structure of **III** was reported in 1995 by Meunier and co-workers using ligand H₂L³ [8]. Subsequently, Che and co-workers

determined the structure of H₂L¹⁶ [24], together with the structures of type-**VI** ligand H₂L⁴⁸ [16] and type-**VII** ligand H₂L⁵⁰ [36].

Fig. 4 shows the structure of H₂L¹⁶. In this structure, both of the *N*-naphthyl-benzylideneamine moieties are essentially planar, with the binaphthyl unit adopting a large dihedral angle of 85.5° [24]. This is similar to the case of H₂L³ [8]. Partial hydrogenation of the binaphthyl unit of H₂L³ to form H₂L⁴⁸ causes very little change in its dihedral angle, and the two halves of H₂L⁴⁸ each remain basically planar. Ligand H₂L⁵⁰ has a slightly larger binaphthyl dihedral angle of 87.6° [36]; the pyridyl and naphthyl groups in each half of the molecule are not coplanar.

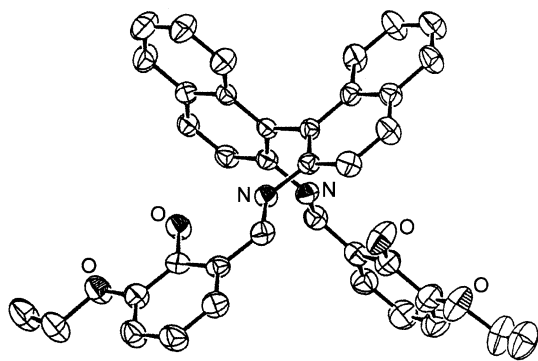


Fig. 4. Crystal structure of binaphthyl Schiff-base ligand H_2L^{16} [24].

3. Synthesis of metal complexes of chiral binaphthyl Schiff-base ligands

By sequential treatment of (R) - H_2L^{22} with t -BuOK and $(Et_4N)_2[NiCl_4]$ in dry *tert*-butyl alcohol, Holm and co-workers prepared (R) - $[Ni(L^{22})]$ [28], which is the first metal complex of chiral binaphthyl Schiff-base ligands **III** reported in the literature.

Up to now, quite a few metal complexes of chiral ligands **III** have been synthesized, with the metal ions spanning Al(III), Cr(III), Mn(II), Mn(III), Fe(II), Fe(III), Co(II), Co(III), Ni(II), Cu(II), Zn(II), Y(III), Zr(IV), Ru(II), and Pd(II) [7,9–16,19–28,30,35,38,40]. The synthetic methods for these complexes and the references are summarized in Table 1. Also included in this table are the syntheses of metal complexes with other chiral binaphthyl Schiff-base ligands **V** and **VI**. Of particular note is the synthesis of (S,S) - $[Cu^{II}(HL^{43})_2]$ and (R,S) - $[Cu_2^{II}(L^{43})_2]$ by Che and co-workers from reactions of $Cu(OAc)_2$ with (S) - and rac - H_2L^{43} , respectively, which highlights the functioning of chirality as a ‘switch’ in selective formation of mono- and di-nuclear metal complexes [35].

Besides the metal complexes shown in Table 1, a series of Ti(IV) complexes of chiral ligands **III**, **V**, and **VI** were generated in situ by treating $Ti(O^iPr)_4$ with (R) - H_2L^n ($n = 1, 3, 4, 6, 7, 11, 13, 14, 21, 25, 43, 46–49$) or (S) - H_2L^6 [13]. These complexes are possibly mononuclear species (R) - or (S) - $[Ti^{IV}(L^n)(O^iPr)_2]$.

Metal complexes of chiral binaphthyl Schiff-base ligands **IV** have been little studied. Only Cu(I) or Cu(II) complexes of **IV** appear in the literature, which were generated in situ from the reactions between $CuOTf$ and (R) -**L**^{34–39}, between $[Cu(MeCN)_4]PF_6$ and (R) -**L**³⁸, or between $Cu(OTf)_2$ and (R) -**L**³⁸ [29].

Notably absent are the complexes of **III–VI** with high-valent transition metal ions (in oxidation states of higher than +4). However, a high-valent transition metal complex of **VII**, (R) - or (S) - $[Os^{VI}(L^{50})(O_2)]$, has been prepared from reaction of (R) - or (S) - H_2L^{50} with $K_2[OsO_2(OH)_4]$ in methanol [36].

4. Structure of metal complexes of chiral binaphthyl Schiff-base ligands

Like the Schiff-base ligands salens, chiral binaphthyl Schiff-base ligands **III** usually function as a dianionic, tetradentate N_2O_2 ligand ($[L^n]^{2-}$) in forming complexes with metal ions, as revealed by the X-ray crystal structure determinations on a number of metal complexes of **III**.

Interestingly, the structures of the four- or six-coordinate species rac - $[Cu^{II}(L^3)]$ [10], rac - $[Cu^{II}(L^n)]$ ($n = 1, 26$) [11], (S) - $[Cu^{II}(L^4)]$ [24], rac - $[Mn^{III}(L^3)(acac)]$ [12], rac - $[Fe^{III}(L^3)(acac)]$ [12], (S) - $[Ru^{II}(L^3)(NO)Cl]$ [13], and rac - $[Al^{III}(L^6)(H_2O)_2]OTf$ [20], determined by the groups of Che, Stack, and Evans, exclusively show nonplanar N_2O_2 arrangements (two of the structures are depicted in Fig. 5). In these cases, the four-coordinate Cu(II) complexes all adopt a distorted tetrahedral configuration whereas the octahedral complexes invariably adopt a *cis*- β -configuration, unlike the corresponding complexes of salens such as $[Cu^{II}(\text{salen})]$ [41] and $[Ru^{II}(\text{salen})(NO)(H_2O)]^+$ [42] which adopt planar configuration and *trans* configuration, respectively. This indicates a significant difference between the coordination modes of ligands **III** and salens.

Table 2 shows the key bond lengths and binaphthyl dihedral angles for some of the foregoing structurally characterized metal complexes of **III**. For the $[M(L^n)]$ moieties indicated in this table ($M = Cu, Mn, Fe, Ru$), the $M-N$ bonds are generally longer than the $M-O$ bonds. The binaphthyl dihedral angles in these complexes fall in the range of 70.2° – 74.8° , except for rac - $[Mn^{III}(L^3)(acac)]$ (whose corresponding binaphthyl dihedral angle is 85.5°). Bearing in mind the binaphthyl dihedral angles of about 85° observed for the free ligands **III**, the coordination of such ligands to Cu(II), Fe(III), and Ru(II) all requires a rotation about the C–C single bond of the binaphthyl unit to reduce its dihedral angle.

Examination of the structures of **III** in more detail might offer a rationalization for the preference of metal complexes of **III** for a nonplanar N_2O_2 arrangement. From the structures of H_2L^3 and H_2L^{16} (Fig. 4), it is evident that (i) the binaphthyl units in **III** would favor large dihedral angles, and (ii) the *N*-naphthyl-benzylideneamine moieties in **III** significantly benefit from electron delocalization over the naphthyl group and the attached benzylideneamine group (note the planarity of the *N*-naphthyl-benzylideneamine moieties in H_2L^3 and H_2L^{16}). These features make the four coordinating atoms (N_2O_2) of $[L^n]^{2-}$ for **III** constrained in a distorted tetrahedral arrangement as depicted in the inset of Fig. 6. Therefore, a four-coordinate metal complex of **III** would prefer a distorted tetrahedral configuration shown in Fig. 6a, rather than a planar configuration shown in Fig. 6b. Likewise, an octahedral

Table 1
Synthesis of metal complexes of chiral binaphthyl Schiff-base ligands **III**, **V**, and **VI**

Complex		Preparation method	Reference
M-L ⁿ	<i>n</i>		
(<i>R</i>)-[Al ^{III} (L ⁿ)Cl] ^a	6	Me ₂ AlX + H ₂ L ⁶	[20]
(<i>R</i>)-[Al ^{III} (L ⁿ)]X (X = OTf, SbF ₆) ^a			
(<i>R</i>)-[Al ^{III} (L ⁿ)(OMe)]	1	AlEt ₃ + H ₂ L ¹ + MeOH	[23,40]
(<i>R</i>)-[Al ^{III} (L ⁿ)(O ⁱ Pr)]	1	Al(OR) ₃ + H ₂ L ¹	[15,23]
(<i>R</i>)-[Ti ^{IV} (L ⁿ)(O ⁱ Pr) ₂]	40	Ti(O ⁱ Pr) ₄ + H ₂ L ⁴⁰	[30]
(<i>R</i>)-[Ti ^{IV} (L ⁿ)(DTBSA)]	40	Ti(O ⁱ Pr) ₄ + H ₂ L ⁴⁰ + H ₂ DTBSA ^b	[30]
(<i>R</i>)-[Cr ^{III} (L ⁿ)Cl]	4	CrCl ₂ + H ₂ L ⁴ + O ₂	[14,27]
(<i>R</i>)- or (<i>S</i>)-[Cr ^{III} (L ⁿ)]X (X = BF ₄ , SbF ₆ , OTf)	3, 4, 6, 23, 27, 28	[Cr ^{III} (L ⁿ)Cl] + AgX	[27]
(<i>S</i>)-[Mn ^{II} (L ⁿ)]	3, 4	Mn(OAc) ₂ ·4H ₂ O + (H ₂ L ⁿ + NaOMe)	[9]
(<i>S</i>)-[Mn ^{II} (L ⁿ)]	1, 6	Mn ₂ (CO) ₁₀ + H ₂ L ⁿ + DBN ^c	[9]
(<i>R</i>)-[Mn ^{III} (L ⁿ)(OAc)]	3, 30	Mn(OAc) ₃ ·2H ₂ O + H ₂ L ⁿ	[12]
(<i>R</i>)-[Mn ^{III} (L ⁿ)(acac)] ^a	3	[Mn(acac) ₃] + H ₂ L ³	[12]
(<i>S</i>)-[Mn ^{III} (L ⁿ) ₂ (OMe) ₂]	3	Mn(OAc) ₃ ·2H ₂ O + H ₂ L ³	[10]
(<i>S</i>)-[Fe ^{II} (L ⁿ)]	3	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O + H ₂ L ³	[9]
(<i>R</i>)-[Fe ^{III} (L ⁿ)(acac)] ^a	3	[Fe(acac) ₃] + (H ₂ L ³ + NaOMe)	[12]
(<i>R</i>)-[Co ^{II} (L ⁿ)]	1, 12		[7]
(<i>S</i>)-[Co ^{II} (L ⁿ)]	3	Co(OAc) ₂ ·4H ₂ O + (H ₂ L ³ + NaOMe)	[9]
(<i>R</i>)-[Co ^{III} (L ⁿ)]SbF ₆	1, 2, 4, 15	(Co(OAc) ₂ + H ₂ L ⁿ) + AgSbF ₆	[22,25]
(<i>R</i>)-[Co ^{III} (L ⁿ)Br]	2		[25]
(<i>R</i>)-[Co ^{III} (L ⁿ)I]	2–5, 32	Co(OAc) ₂ + H ₂ L ⁿ + I ₂	[25]
(<i>R</i>)-[Ni ^{II} (L ⁿ)]	22	(Et ₄ N) ₂ [NiCl ₄] + (H ₂ L ²² + ^t BuOK)	[28]
(<i>S</i>)-[Ni ^{II} (L ⁿ)]	3, 4	Ni(OAc) ₂ ·2H ₂ O + (H ₂ L ⁿ + NaOMe)	[9]
(<i>S</i>)-[Cu ^{II} (L ⁿ)]	1, 3–6, 9–11, 16, 18, 21, 25, 30, 32	Cu(OAc) ₂ + H ₂ L ⁿ	[10,21] ^d [24,38]
(<i>S</i>)-[Cu ^{II} (L ⁿ)]	6	CuCl ₂ + H ₂ L ⁶	[19]
(<i>S</i>)-[Cu ^{II} (L ⁿ)]	3, 4	CuCl ₂ + (H ₂ L ⁿ + NaOMe)	[9]
<i>Rac</i> -[Cu ^{II} (L ⁿ)]	1, 6, 8, 17, 26, 27	Cu(OAc) ₂ + H ₂ L ⁿ	[11]
(<i>S,S</i>)-[Cu ^{II} (HL ⁿ) ₂]	43	Cu(OAc) ₂ + H ₂ L ⁴³	[35]
(<i>R,S</i>)-[Cu ^{II} (L ⁿ) ₂]	43	Cu(OAc) ₂ + H ₂ L ⁴³	[35]
(<i>S</i>)-[Zn ^{II} (L ⁿ)]	3	Zn(OAc) ₂ ·2H ₂ O + (H ₂ L ³ + NaOMe)	[9]
(<i>R</i>)-[Y ^{III} (L ⁿ)(OCH ₂ CH ₂ -NMe ₂)]	1	Y(OCH ₂ CH ₂ NMe ₂) ₃ + H ₂ L ¹	[15]
(<i>R</i>)-[Zr ^{IV} (L ⁿ)(OPh) ₂]	1	{[ZrCl ₄ (THF) ₂] + Na ₂ L ¹ } + LiOPh	[26]
(<i>S</i>)-[Ru ^{II} (L ⁿ)(NO)Cl]	3	[Ru ^{II} (NO)Cl ₃ (PPh ₃) ₂] + (H ₂ L ³ + NaH)	[13]
(<i>R</i>)-[Pd ^{II} (L ⁿ)]	3 ^a , 48	Pd(OAc) ₂ + (H ₂ L ⁿ + NaOMe)	[16]

^a Racemic complex was also prepared.

^b H₂DTBSA = 3,5-di-*tert*-butyl-salicylic acid.

^c DBN = 1,5-diazabicyclo[4.3.0]non-5-ene.

^d (*R*)-[Cu^{II}(L¹)].

metal complex of **III** would prefer the *cis*-configurations shown in Fig. 6c (*cis*-β) and Fig. 6d (*cis*-α), rather than the *trans*-configuration shown in Fig. 6e (which has a planar N₂O₂ arrangement). This is in contrast to the corresponding metal complexes of salens, in which cases the planar N₂O₂ arrangements can be readily maintained, and both the planar four-coordinate species and the *trans*-octahedral species are very common [43].

The structures of four- or six-coordinate species *rac*-[Pd^{II}(L³)] (Fig. 7) [16], (*R*)-[Pd^{II}(L⁴⁸)] [16], and (*R*)-[Co^{II}(L³)(DMSO)₂] [44] recently determined by Che and co-workers provide unusual cases in which the [Lⁿ]²⁻ ligands of **III** and its analogue **VI** bind metal ions with basically planar N₂O₂ arrangement. These complexes have similar binaphthyl dihedral angles (ca. 70°–74°) to those of their nonplanar N₂O₂ analogues (see Table 2).

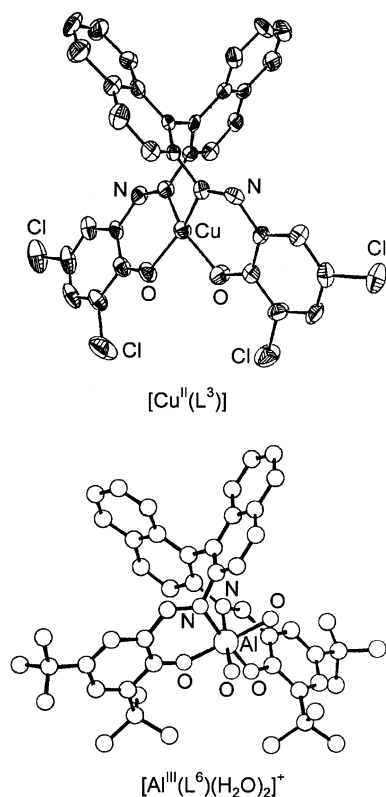


Fig. 5. Crystal structures of $[\text{Cu}^{\text{II}}(\text{L}^3)]$ [10] and $[\text{Al}^{\text{III}}(\text{L}^6)(\text{H}_2\text{O})_2]\text{OTf}$ [20] (the counteranion of the latter is not shown).

However, each pair of their naphthyl group and the attached benzylideneimine group is nearly perpendicular to one another, indicating that the planar N_2O_2 arrangement is maintained at the expense of almost full break of the electron delocalization over naphthyl group and the attached benzylideneimine group. It is unclear why the $\text{Co}(\text{II})$ complex adopts such an unusual configuration. The basically planar N_2O_2 arrangements in the two $\text{Pd}(\text{II})$ complexes might stem from a strong

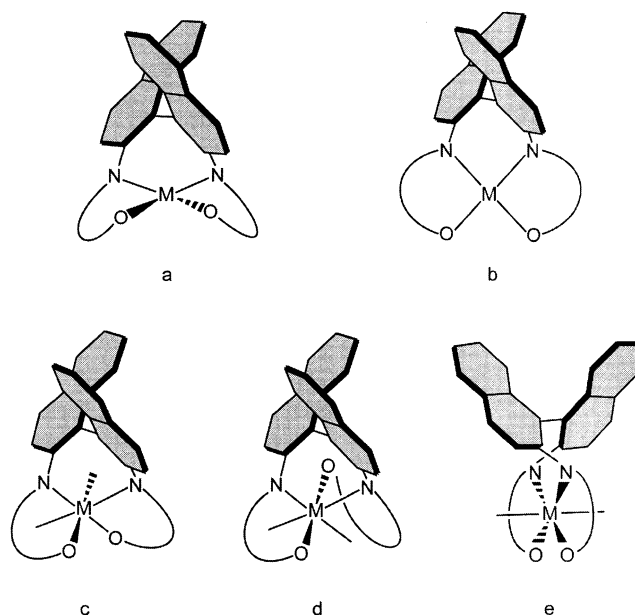
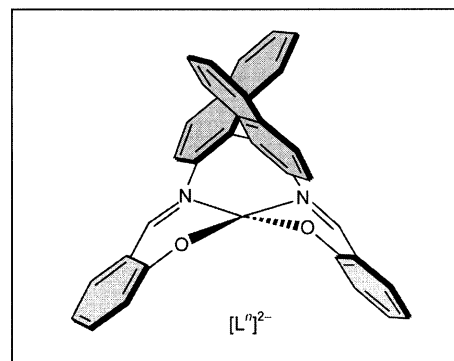


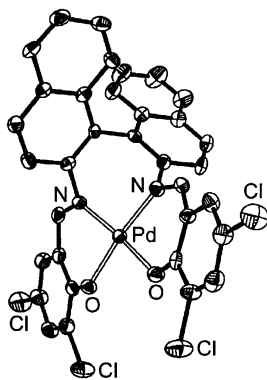
Fig. 6. Possible geometric configurations of four-coordinate and octahedral metal complexes of **III**. The inset shows the configuration of $[\text{L}^n]^{2-}$ for **III** (H_2L^n) derived from X-ray crystal structure determinations.

Table 2

Key bond lengths and binaphthyl dihedral angles in the X-ray crystal structures of some metal complexes of binaphthyl Schiff-base ligands **III**

Complex	$[\text{M}(\text{L}^n)]$ moiety		Binaphthyl dihedral angle ($^\circ$)	Other bond lengths (\AA)	Reference
	M–N (\AA)	M–O (\AA)			
<i>rac</i> - $[\text{Cu}^{\text{II}}(\text{L}^3)]$	1.952(5) ^a 1.954(5) ^a	1.890(5) ^a 1.890(5) ^a	74.8 ^a		[10]
(<i>S</i>)- $[\text{Cu}^{\text{II}}(\text{L}^4)]$	1.963(7) 1.912(7)	1.899(6) 1.907(6)	72.49		[24]
<i>rac</i> - $[\text{Mn}^{\text{III}}(\text{L}^3)(\text{acac})]$	2.056(8) 2.277(7)	1.896(7) 1.887(6)	85.5	Mn–O(acac): 1.915(7), 2.124(7)	[12]
<i>rac</i> - $[\text{Fe}^{\text{III}}(\text{L}^3)(\text{acac})]$	2.168(5) ^a 2.147(5) ^a	1.944(4) ^a 1.915(4) ^a	72.1	Fe–O(acac): 2.016(5), 1.997(5) ^a	[12]
(<i>S</i>)- $[\text{Ru}^{\text{II}}(\text{L}^3)(\text{NO})\text{Cl}]$	2.046(6) 2.075(6)	1.974(5) 2.040(5)	70.2	Ru–NO: 1.724(7) Ru–Cl: 2.365(2)	[13]

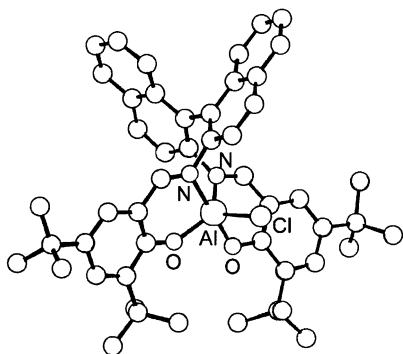
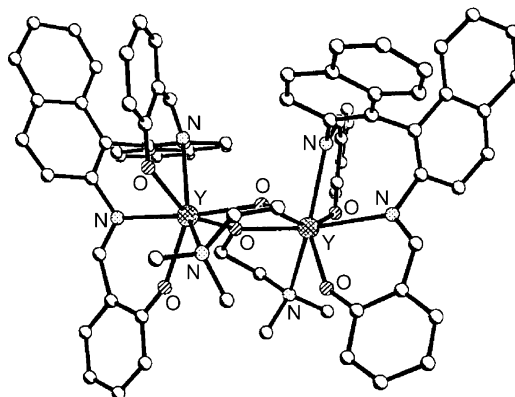
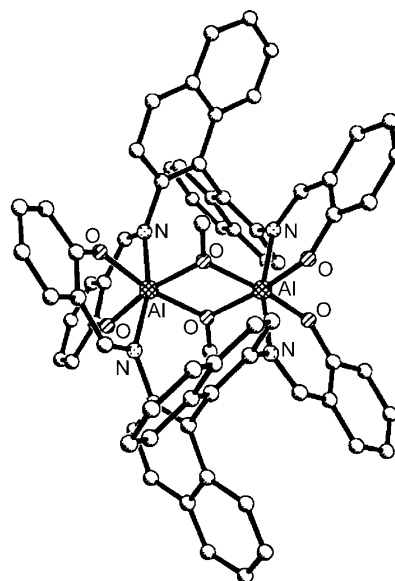
^a Average value of two independent molecules.

Fig. 7. Crystal structure of $[\text{Pd}^{\text{II}}(\text{L}^3)]$ [16].

preference of $\text{Pd}(\text{II})$ ion for a square planar configuration [16]. The enhanced stability resulting from the pseudo-square planar coordination of the $\text{Pd}(\text{II})$ ion to $[\text{L}^{3/48}]^{2-}$ probably well compensates the energy required to break the above electron delocalization present in the free ligands.

Evans and co-workers found that the crystal structure of $\text{rac}-[\text{Al}^{\text{III}}(\text{L}^6)\text{Cl}]$ contains a five-coordinate metal center [20], as shown in Fig. 8. As usual, the ligand $[\text{L}^6]^{2-}$ in this complex exhibits a non-planar N_2O_2 arrangement, with the $\text{AlN}_2\text{O}_2\text{Cl}$ core adopting a distorted trigonal bipyramidal configuration. Similar distorted trigonal bipyramidal configuration has also been observed by Che and co-workers in the crystal structure of $\text{rac}-[\text{Co}^{\text{II}}(\text{L}^3)(\text{H}_2\text{O})]$ [44]. The binaphthyl dihedral angles of these five-coordinate $\text{Al}(\text{III})$ and $\text{Co}(\text{II})$ complexes are 62° and 64.1° , respectively, which are considerably smaller than those of the four- and six-coordinate metal complexes described above.

Recently, Coates and co-workers determined the structure of $(R,R)-[\text{Y}^{\text{III}}(\text{L}^1)(\text{OCH}_2\text{CH}_2\text{NMe}_2)]$ by X-ray crystallography [23]. This complex exists as a dimer doubly-bridged by the oxygen atoms of the $\text{Me}_2\text{NCH}_2\text{CH}_2\text{O}^-$ alkoxide groups, as shown in Fig. 9. The nitrogen atoms of the bridging $\text{Me}_2\text{NCH}_2\text{CH}_2\text{O}^-$ groups are also bound to the $\text{Y}(\text{III})$ ions, making each $\text{Y}(\text{III})$ center to be seven-coordinate.

Fig. 8. Crystal structure of $[\text{Al}^{\text{III}}(\text{L}^6)\text{Cl}]$ [20]. $(R,R)-[\text{Y}^{\text{III}}(\text{L}^1)(\text{OCH}_2\text{CH}_2\text{NMe}_2)]_2$  $(R,R)-[\text{Al}^{\text{III}}_2(\text{L}^1)_2(\text{OMe})_2]$ Fig. 9. Crystal structures of $(R,R)-[\text{Y}^{\text{III}}(\text{L}^1)(\text{OCH}_2\text{CH}_2\text{NMe}_2)]_2$ and $(R,R)-[\text{Al}^{\text{III}}_2(\text{L}^1)_2(\text{OMe})_2]$ [23].

Interestingly, from the methanol mother liquor for preparation of $(R)-[\text{Al}^{\text{III}}(\text{L}^1)(\text{OMe})]$, Coates and co-workers obtained a dinuclear $\text{Al}(\text{III})$ complex, $(R,R)-[\text{Al}^{\text{III}}_2(\text{L}^1)_2(\text{OMe})_2]$ [23], whose crystal structure (Fig. 9) uniquely contains bridging binaphthyl Schiff-base ligands **III**. The two $\text{Al}(\text{III})$ ions in the complex are also doubly-bridged by the oxygen atoms of the MeO^- alkoxide groups, with the geometry of the $\text{M}(\mu_2\text{-OR})_2\text{M}$ unit similar to that of the dimer of $(R)-[\text{Y}^{\text{III}}(\text{L}^1)(\text{OCH}_2\text{CH}_2\text{NMe}_2)]$.

Structurally characterized metal complexes of binaphthyl Schiff-base ligands **V** are rare. Carreira and co-workers proposed that complexes $(R)[\text{Ti}^{\text{IV}}(\text{L}^{40})-(\text{O}^i\text{Pr})_2]$ and $(R)-[\text{Ti}^{\text{IV}}(\text{L}^{40})(\text{DTBSA})]$ ($\text{H}_2\text{DTBSA} = 3,5\text{-di-tert-butyl-salicylic acid}$) are mononuclear species containing five-coordinate $\text{Ti}(\text{IV})$ ions. Recently, Che

and co-workers reported the X-ray crystal structures of mononuclear complex (S,S) - $[\text{Cu}^{\text{II}}(\text{HL}^{43})_2]$ and dinuclear complex (R,S) - $[\text{Cu}_2^{\text{II}}(\text{L}^{43})_2]$ [35], which contain bidentate $[\text{HL}^{43}]^-$ and tridentate $[\text{L}^{43}]^{2-}$ ligands, respectively (Fig. 10). In the mononuclear species (S,S) - $[\text{Cu}^{\text{II}}(\text{HL}^{43})_2]$, the OH groups attached to the binaphthyl units remain uncoordinated, whereas in the dinuclear species (R,S) - $[\text{Cu}_2^{\text{II}}(\text{L}^{43})_2]$, all such groups are deprotonated and function as a bridge connecting two Cu(II) ions. The dihedral angles of the binaphthyl units in the two Cu(II) complexes fall in the range of 72° – 84° .

The structure of the dioxo osmium(VI) complex of chiral ligand **VII**, (R) - $[\text{Os}^{\text{VI}}(\text{L}^{50})(\text{O}_2)]$, has also been determined [36], which is shown in Fig. 11. This high-valent metal complex has a distorted octahedral configuration with the four coordinating nitrogen atoms of $[\text{L}^{50}]^{2-}$ adopting a basically planar arrangement. The Os=O distances are found to be 1.726(6) and 1.727(5) Å. Formation of (R) - $[\text{Os}^{\text{VI}}(\text{L}^{50})(\text{O}_2)]$ from the free H_2L^{50} ligand significantly reduces the dihedral angle between the naphthyl planes ($87.6^\circ \rightarrow 71.2^\circ$), like the formation of most metal complexes from ligands **III**.

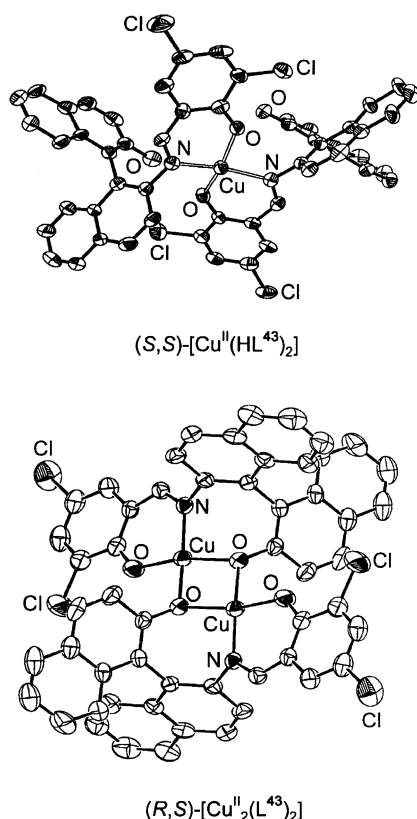


Fig. 10. Crystal structures of (S,S) - $[\text{Cu}^{\text{II}}(\text{HL}^{43})_2]$ and (R,S) - $[\text{Cu}_2^{\text{II}}(\text{L}^{43})_2]$ [35].

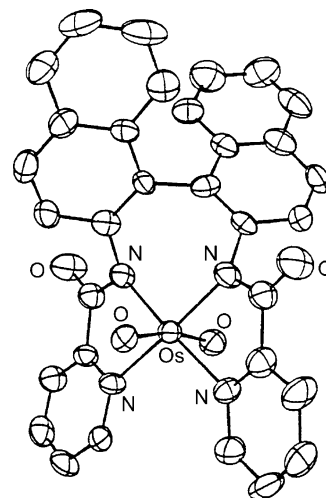


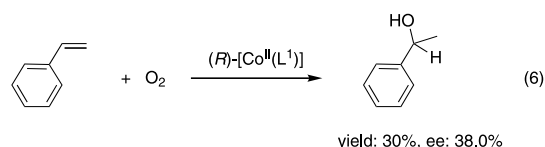
Fig. 11. Crystal structure of (R) - $[\text{Os}^{\text{VI}}(\text{L}^{50})(\text{O}_2)_2]$ [36].

5. Application of metal complexes of chiral binaphthyl Schiff-base ligands in stereoselective organic transformations

5.1. Hydroxylation of styrene

Enantioselective hydroxylation of styrene was the first organic reaction to involve a metal complex of a binaphthyl Schiff-base ligand as a catalyst. In 1988, Nishinaga and co-workers reported that (R) - $[\text{Co}^{\text{II}}(\text{L}^n)]$ ($n = 1, 12$) can catalyze hydroxylation of styrene with dioxygen [7]. The reactions were conducted in the presence of alcohol, affording optically active 1-phenylethanol in 30% yield and 38.0% ee in the case of more efficient catalyst (R) - $[\text{Co}^{\text{II}}(\text{L}^1)]$ (reaction (6) in Scheme 3). This enantioselectivity is considerably higher than that (2.1% ee) obtained by using a chiral $[\text{Co}(\text{salen})]$ -type catalyst formed, formally, by replacing the 1,1'-binaphthyl group of (R) - $[\text{Co}^{\text{II}}(\text{L}^{12})]$ with a 1,2-cyclohexyl group [7].

A Co(III) hydride intermediate, (R) - $[\text{Co}^{\text{III}}(\text{L}^1)\text{H}]$, was proposed to be involved in reaction (6) by Nishinaga and co-workers [7]. They postulated that addition of the hydride species to styrene might form (R) - $[\text{Co}^{\text{III}}(\text{L}^1)(\text{CH}(\text{Me})\text{Ph})]$, which possibly reacts with dioxygen to give (R) - $[\text{Co}^{\text{III}}(\text{L}^1)(\text{OOCH}(\text{Me})\text{Ph})]$. Attack of the coordinated $\text{OOCH}(\text{Me})\text{Ph}$ group by alcohol would generate the hydroperoxide $\text{HOOCH}(\text{Me})\text{Ph}$, whose asymmetric decomposition promoted by (R) -



Scheme 3.

[Co^{II}(L¹)] is probably responsible for the formation of optically active 1-phenylethanol [7].

5.2. Aldol reactions

Aldol reactions are the most extensively studied organic transformations catalyzed by metal complexes of binaphthyl Schiff-base ligands. Carreira and co-workers reported the first examples of such catalytic system in 1994 [30]. They found that complex (R)-[Ti^{IV}(L⁴⁰)(OⁱPr)₂] catalyzes the aldol addition reaction of benzaldehyde and *O*-trimethylsilyl *O*-ethyl ketene acetal (CH₂=C(OEt)OSiMe₃) to give a mixture of aldol products PhCH(X)CH₂CO₂Et in 12 (X = OH) and 68% (X = OSiMe₃) yields with good enantioselectivity (X = OH: 78% ee, X = OSiMe₃: 64% ee). The catalytic efficiency of (R)-[Ti^{IV}(L⁴⁰)(OⁱPr)₂] increases substantially upon replacing the ⁱPrO[−] group of the catalyst with a salicylate group. For example, reaction of benzaldehyde with CH₂=C(OR)OSiMe₃ in the presence of 2–5 mol.% of (R)-[Ti^{IV}(L⁴⁰)(DTBSA)] affords the silylated adduct PhCH(OSiMe₃)CH₂CO₂R in 91 (R = Me) and 94% (R = Et) yield.

Complex (R)-[Ti^{IV}(L⁴⁰)(DTBSA)] is an excellent catalyst for aldol addition reactions of CH₂=C(OMe)OSiMe₃, CH₂=C(OEt)OSiMe₃ [30] and dienolate [32,33] with a variety of aldehydes, as reported by Carreira and co-workers (reactions (7) and (8) in Scheme 4). However, for the aldol addition reactions between CH₂=C(OMe)Me and aldehydes (reaction (9) in Scheme 4), the simpler complex (R)-[Ti^{IV}(L⁴⁰)(OⁱPr)₂] also exhibits high catalytic efficiency [31]. These (R)-[Ti^{IV}(L⁴⁰)(DTBSA)]- or (R)-[Ti^{IV}(L⁴⁰)(OⁱPr)₂]-catalyzed aldol addition reactions feature product yields of 95–99% for aldehydes **4** (reactions (8) and (9)), **7/9** (reaction (9)), and **11/12** (reaction (8)). Enantiomeric excesses of 90–98% have been achieved for all the aldehydes shown in Scheme 4 except **3** (reaction (7), R' = Et), **4** (reactions (7) (R' = Et) and (9)), **5** (reactions (8) and (9)), and **6** (reaction (9)).

The above aldol addition reactions between dienolate and aldehydes catalyzed by (R)-[Ti^{IV}(L⁴⁰)(DTBSA)] (reaction (8) in Scheme 4) provide direct access to optically active protected acetoacetate adducts, which are key intermediates in the total synthesis of some biologically active natural products. For example, the total synthesis of macrolactin A reported by Carreira and co-workers [33] involves synthesis of the optically active aldol addition products of reaction (8) for **13**.

To facilitate separation of the catalyst or product for the catalytic aldol addition reactions between silyl ketene acetals and aldehydes, Salvadori and co-workers prepared a chiral soluble polymer derived from (R)-H₂L⁴², styrene, and 1,4-divinylbenzene [34]. They observed that the complex formed in situ from treatment of such a chiral polymer with Ti(OⁱPr)₄ catalyzes the

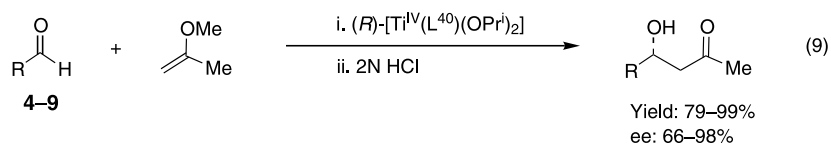
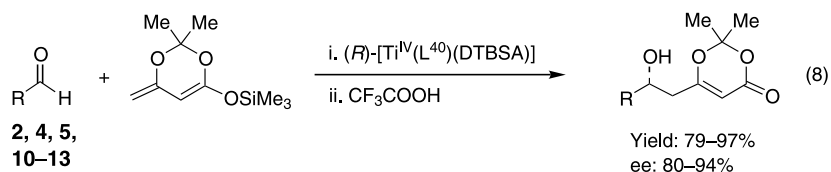
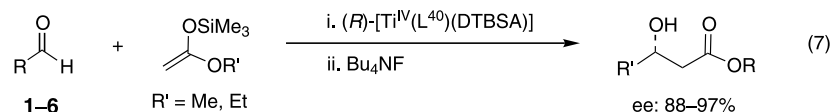
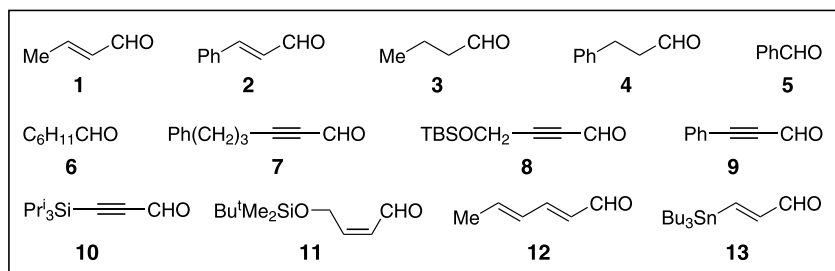
aldol addition reaction of CH₂=C(OCH₂Ph)OSiMe₃ and benzaldehyde to give (R)-PhCH(OH)CH₂-CO₂CH₂Ph in 26% ee with 32% substrate conversion. The catalytic system, upon addition of pentane, can be easily separated from the reaction mixture by filtration.

Recently, Evans and co-workers employed complexes (R)-[Al^{III}(L⁶)(H₂O)₂]OTf and (R)-[Al^{III}(L⁶)]SbF₆ to catalyze aldol addition/acyl transfer reactions between 5-methoxyoxazole and aldehydes [20]. Treatment of 5-methoxyoxazole with benzaldehyde in the presence of catalyst (R)-[Al^{III}(L⁶)(H₂O)₂]OTf affords the corresponding (4*S*,5*S*)-oxazoline product with excellent enantioselectivity (98% ee) and *cis*-selectivity (*cis:trans* ratio = 93:7). A problem in the (R)-[Al^{III}(L⁶)(H₂O)₂]-OTf-catalyzed reaction lies in the turnover (only 60% conversion was obtained). By employing catalyst (R)-[Al^{III}(L⁶)]SbF₆, the reaction between 5-methoxyoxazole and benzaldehyde proceeds to a considerably higher conversion of 80% without lowering the enantio- and diastereo-selectivity. Remarkably, complex (R)-[Al^{III}(L⁶)]SbF₆ can also catalyze the reactions of 5-methoxyoxazole with a wide range of aromatic aldehydes to give optically active *cis*-oxazoline adducts with excellent enantioselectivity (91 to >99% ee, reaction (10) in Scheme 5) [20]. The isolated yields of oxazoline adducts reach 90–100% except for **14e**, **17b**, and **19**. For aldehydes **17a** and **17b**, almost complete diastereoselectivity (*cis:trans* ratio > 99:1) has been achieved.

5.3. Alkene epoxidation

Epoxidation of alkenes catalyzed by metal complexes of chiral binaphthyl Schiff-base ligands was first reported by the groups of Meunier [9] and Che [10] in 1996. Meunier and co-workers found that epoxidations of 1,2-dihydronaphthylene (**23**) with NaClO catalyzed by (S)-[Mn^{II}(L^{*n*})] (*n* = 1, 3, 4) afford the epoxide in 13–15% ee [9] (reaction (11) in Scheme 6), which are similar to the ee value of 13% obtained for a [Mn^{II}(salen)]-type catalyst that contains the 1,2-cyclohexyl analogue of L⁴. However, they observed that complex (S)-[Mn^{II}(L⁶)] is much less efficient than its 1,2-cyclohexyl analogue in catalyzing the NaClO epoxidation of **23**. Che and co-workers studied the epoxidation of *cis*-β-methylstyrene (**24**) and 4-chlorostyrene (**25**) with PhIO by employing manganese catalysts formed in situ from Mn(OAc)₃·*x*H₂O and (S)-H₂L^{*n*} (*n* = 3, 11, 29–33) (reaction (12) in Scheme 6), of which the catalyst formed from (S)-H₂L³⁰ was found to give the highest enantiocontrol (up to 58% ee) [10]. They also examined the epoxidation of styrene (**26**), 3-chlorostyrene (**27**), 3-nitrostyrene (**28**), and 4-methylstyrene (**29**) with PhIO catalyzed by 'Mn(OAc)₃·*x*H₂O + (S)-H₂L⁶', which afford the epoxides in 35–49% ee [10].

In a subsequent work by Che and co-workers [12], isolated and well-characterized complexes (R)-[Mn^{III}(L-

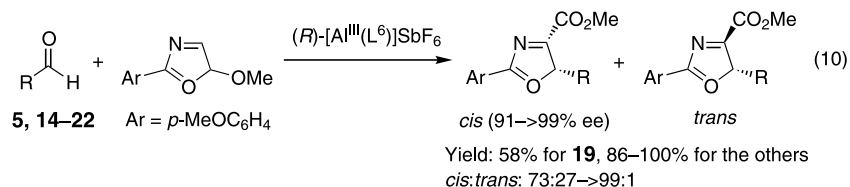
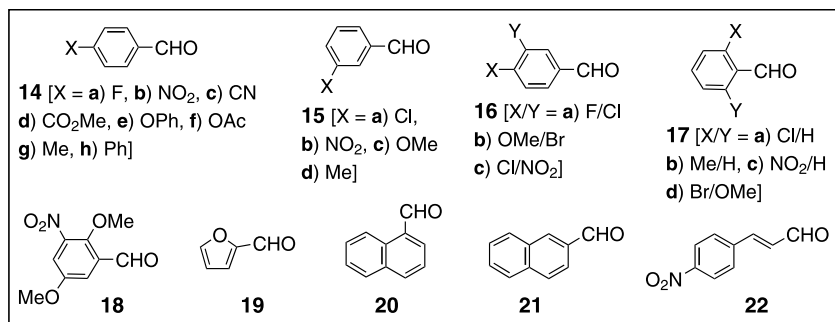


Scheme 4.

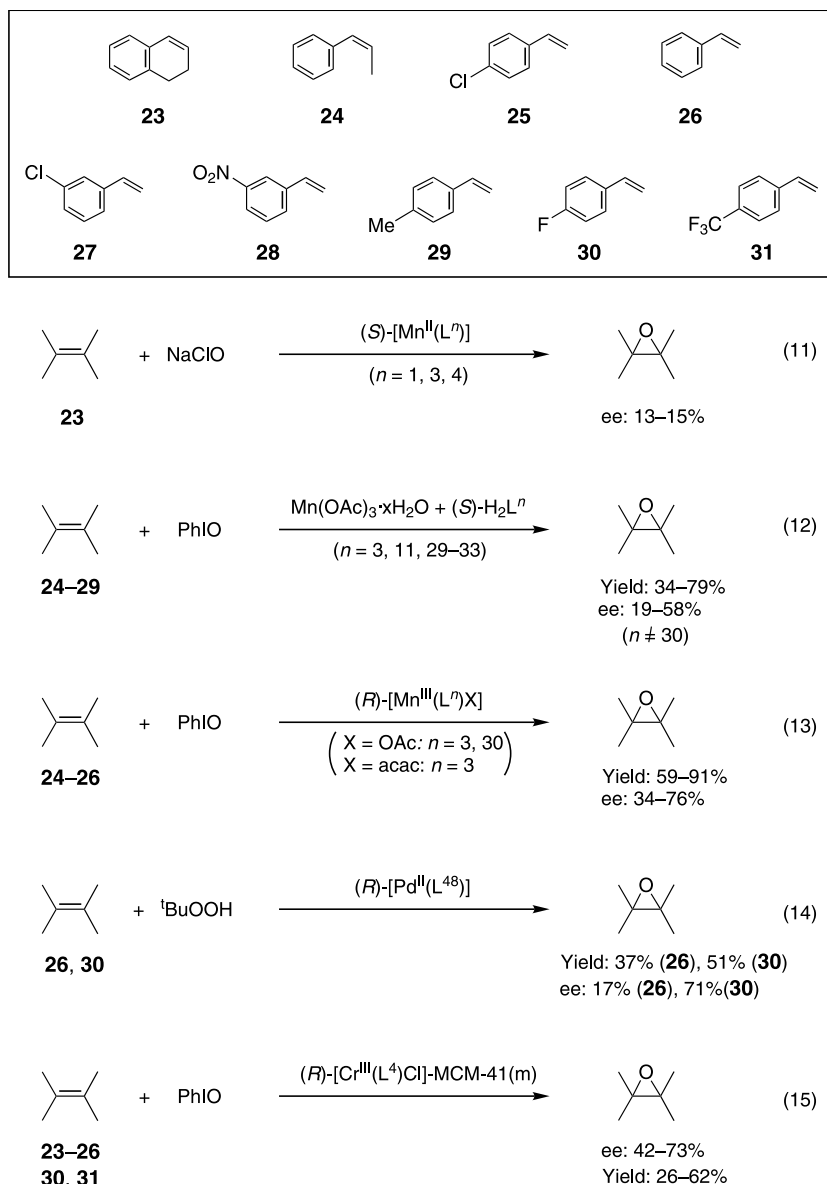
ⁿ)(OAc)] and (R)-[Mn^{III}(L³)(acac)] were shown to be active catalysts for the PhIO epoxidation of styrenes (reaction (13) in Scheme 6). The epoxidations of **26** catalyzed by (R)-[Mn^{III}(Lⁿ)(OAc)] (*n* = 3, 28) give styrene oxide in the yields and ee's very similar to those observed for the corresponding 'Mn(OAc)₃·*x*H₂O + (S)-H₂Lⁿ' systems under identical conditions. When

the epoxidation of **24** catalyzed by (R)-[Mn^{III}(L³⁰)(OAc)] was conducted in a low-polarity solvent (toluene) at low temperature (−20 °C), *cis*-β-methylstyrene oxide was obtained in 76% ee [12].

Complexes (R)-[Pd^{II}(Lⁿ)] (*n* = 3, 48) reported by Che and co-workers can also catalyze alkene epoxidations [16]. The reactions of styrene and 4-fluorostyrene (**30**)



Scheme 5.



Scheme 6.

with ^tBuOOH in the presence of catalyst (*R*)-[Pd^{II}(L⁴⁸)] afforded the corresponding epoxides in 17 and 71% ee, respectively (reaction (14) in Scheme 6). This is the first enantioselective alkene epoxidation catalyzed by a palladium complex.

Epoxidation of alkenes catalyzed by (*R*)-[Cr^{III}(L⁴)Cl]-MCM-41(m), the unique example of heterogenized metal catalysts bearing chiral binaphthyl Schiff-base ligands, has also been reported [14]. This heterogenized catalyst was prepared by Che and co-workers by treating (*R*)-[Cr^{III}(L⁴)Cl] with modified MCM-41. Reactions of PhIO with alkenes **23–26**, **30**, and 4-trifluoromethylstyrene (**31**) in the presence of catalyst (*R*)-[Cr^{III}(L⁴)Cl]-MCM-41(m) produced the respective epoxides in 42–73% ee [14] (reaction (15) in Scheme 6). The catalyst can be reused at least two times without

decrease in enantioselectivity, in contrast to the decrease of enantioselectivity by 40% ee observed for the first-time reuse of a heterogenized Mn–salen–MCM-41 catalyst [45]. Even more interesting is that, although heterogenization of a homogenous catalyst usually reduces its enantioselectivity, the heterogenized catalyst (*R*)-[Cr^{III}(L⁴)Cl]-MCM-41(m) gives significantly higher enantioselectivity than the homogeneous catalyst (*R*)-[Cr^{III}(L⁴)Cl] in catalyzing epoxidation of **24** with PhIO [14].

5.4. Alkene cyclopropanation

Suga et al. reported that Cu(I) or Cu(II) complexes formed in situ from reactions of CuOTf with (*R*)-Lⁿ ($n = 34–39$), or from reactions of [Cu(MeCN)₄]PF₆ and

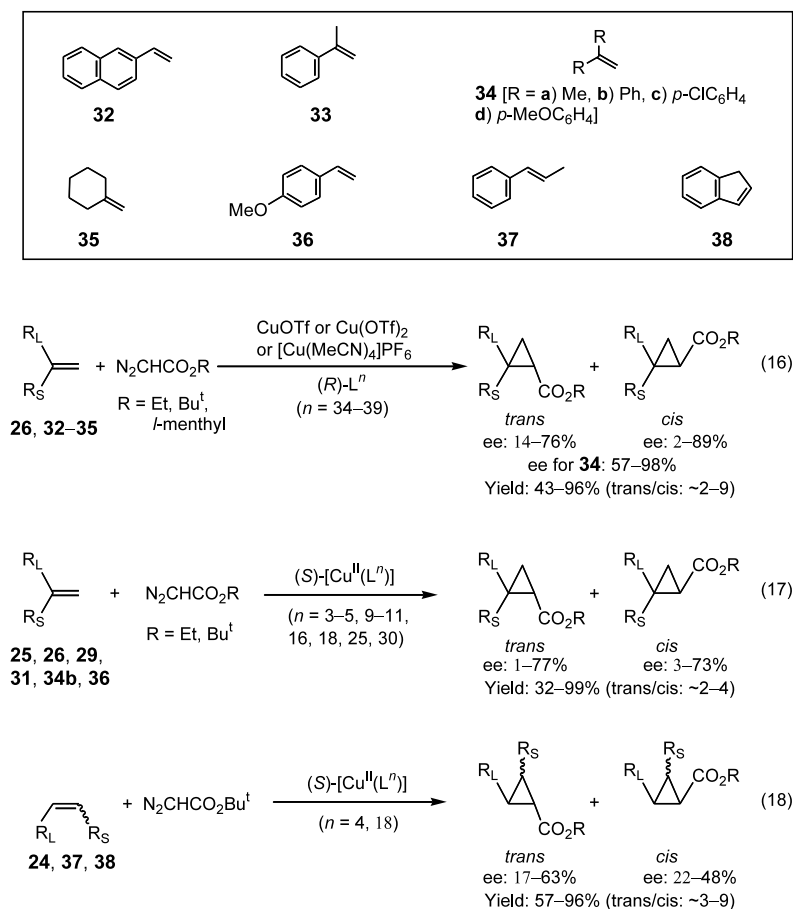
$\text{Cu}(\text{OTf})_2$ with $(R)\text{-L}^{38}$, catalyze the cyclopropanation of several terminal alkenes with diazoacetates $\text{N}_2\text{CHCO}_2\text{R}$ ($\text{R} = \text{Et}$, $t\text{-Bu}$, $l\text{-menthyl}$) to afford cyclopropanes in 60–96% yields (except for the alkene **34d**) with *trans*:*cis* ratio ranging from 69:31 to 90:10 [29] (reaction (16) in Scheme 7). The ee values obtained for the cyclopropanes derived from alkenes **26**, **32**, and **33** range from 14 to 76% for the *trans* isomers and from 2 to 89% for the *cis* isomers. The cyclopropanations of diaryl substituted terminal alkenes **34b–d** with $l\text{-menthyl}$ diazoacetate catalyzed by ' $(R)\text{-L}^{38} + \text{CuOTf}$ or $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ ' give the cyclopropanes in excellent enantioselectivities (90–98% ee).

Che and co-workers examined the catalytic properties of isolated complexes $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^n)]$ ($n = 3\text{--}6, 9\text{--}11, 16, 18, 21, 25, 30, 32$) toward cyclopropanation of styrene with $\text{N}_2\text{CHCO}_2\text{R}$ ($\text{R} = \text{Et}$, $t\text{-Bu}$) [24]. These $\text{Cu}(\text{II})$ complexes, except $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^6)]$, $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^{21})]$, and $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^{32})]$, are all active in catalyzing the styrene cyclopropanation, producing the cyclopropanes in 32–99% yields with *trans*:*cis* ratio ranging from 65:35 to 80:20 (reaction (17) in Scheme 7). The cyclopropanation with $\text{N}_2\text{CHCO}_2^t\text{Bu}$ catalyzed by $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^{18})]$ gives ee values of 74 and 73% for the resulting *trans* and *cis* cyclopropanes, respectively. Complexes $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^{18})]$

and $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^4)]$ have also been used to catalyze the $\text{N}_2\text{CHCO}_2^t\text{Bu}$ cyclopropanation of various aromatic alkenes (reactions (17) and (18) in Scheme 7) [24]. In the presence of these catalysts, even non-terminal alkenes **24**, **37**, and **38** can be cyclopropanated in 57–96% yields with *trans*:*cis* ratio of up to 90:10 (ee: 17–63% for *trans* isomers, 22–48% for the *cis* isomers).

5.5. Trimethylsilylcyanation of aldehydes

The titanium complexes formed in situ from reactions of $\text{Ti}(\text{O}^i\text{Pr})_4$ with $(R)\text{-H}_2\text{L}^n$ ($n = 1, 3, 4, 6, 11, 13, 14, 21, 25, 43, 46\text{--}49$) or $(S)\text{-H}_2\text{L}^6$ can catalyze trimethylsilylcyanation of benzaldehyde, as reported by Che and co-workers, affording cyanohydrins in 42–98% yields and 24–93% ee upon treatment with acid (reaction (19) in Scheme 8) [13]. Of these ' $\text{Ti}(\text{O}^i\text{Pr})_4 + (R)\text{-}$ or $(S)\text{-H}_2\text{L}^n$ ' catalytic systems, the ' $\text{Ti}(\text{O}^i\text{Pr})_4 + (R)\text{-}$ or $(S)\text{-H}_2\text{L}^6$ ' system was found to be the most efficient, which gives cyanohydrins in ~94 yields with 93% ee. An isolated ruthenium complex bearing $[\text{L}^3]^{2-}$ ligand ($(S)\text{-}[\text{Ru}^{\text{II}}(\text{L}^3)(\text{NO})\text{Cl}]$), upon treatment with AgPF_6 , can also catalyze the same reaction with 90% yield, but the enantioselectivity obtained is low (24% ee) [13]. Trimethylsilylcyanations of other aldehydes indicated in



Scheme 7.

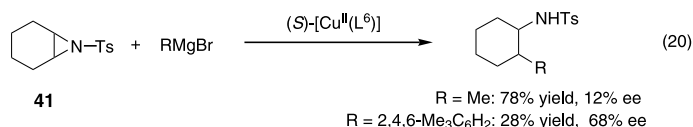
Scheme 8 in the presence of catalyst $\text{Ti}(\text{O}^i\text{Pr})_4 + (R)\text{-H}_2\text{L}^6$ produce the corresponding cyanohydrins in 63–87% yields with up to 96% ee [13].

5.6. Desymmetrization of meso-*N*-sulfonylaziridine

Müller and co-workers have investigated the catalytic properties of $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^6)]$ toward the desymmetrization of 7-tosyl-7-azabicyclo[4.1.0]heptane (**41**) with Grignard reagent RMgBr ($\text{R} = \text{Me}$ and 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$) [19] (reaction (20) in **Scheme 9**). The desymmetrization of **41** with MeMgBr affords a sulfonamide product in 78% yield and 12% ee, very similar to the yield and ee value for the same reaction catalyzed by the 1,2-cyclohexyl analogue of $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^6)]$. However, for the desymmetrization with (2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$) MgBr , catalyst $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^6)]$ results in a substantially higher enantioselectivity than its 1,2-cyclohexyl analogue (68 vs. 12% ee), although the latter affords the product in a substantially higher yield (28 vs. 75%) [19].

5.7. Baeyer-Villiger oxidation of aryl cyclobutanone

Baeyer-Villiger oxidation transforms a carbonyl group to an ester group. Katsuki and co-workers reported that complexes $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^n)]\text{SbF}_6$ ($n = 1, 2, 4$) and $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^n)]\text{I}$ ($n = 2, 32$) are active catalysts for Baeyer-Villiger oxidation of 3-phenyl cyclobutanone (**42**) with H_2O_2 or urea hydrogen peroxide adduct (UHP) (reaction (21) in **Scheme 10**) [22,25]. These reactions afforded $(S)\text{-}3\text{-phenylbutano-4-lactone}$ in up to 69% ee when they were conducted in dichloromethane. In contrast, no asymmetric induction has been observed by using the 1,2-cyclohexyl analogue of $[\text{Co}^{\text{III}}(\text{L}^4)]\text{SbF}_6$ as a catalyst (although it can also catalyze the reaction). Polar solvents such as ethers and alcohols significantly improve the efficiency of catalysts $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^2)]\text{SbF}_6$ and $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^2)]\text{I}$. Under such conditions, the desired lactone can be formed in 52–97% yields with 60–79% ee, an enantioselectivity significantly higher than that (40–47% ee) attained by



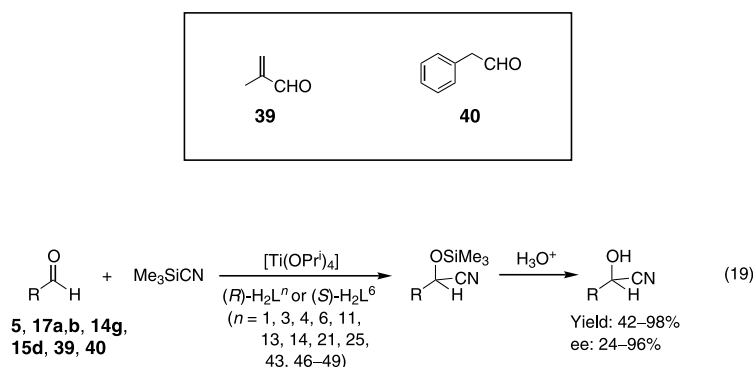
Scheme 9.

employing other types of chiral transition metal complex catalysts [22,25] except $[\text{Zr}(\text{salen})]$ catalysts [26].

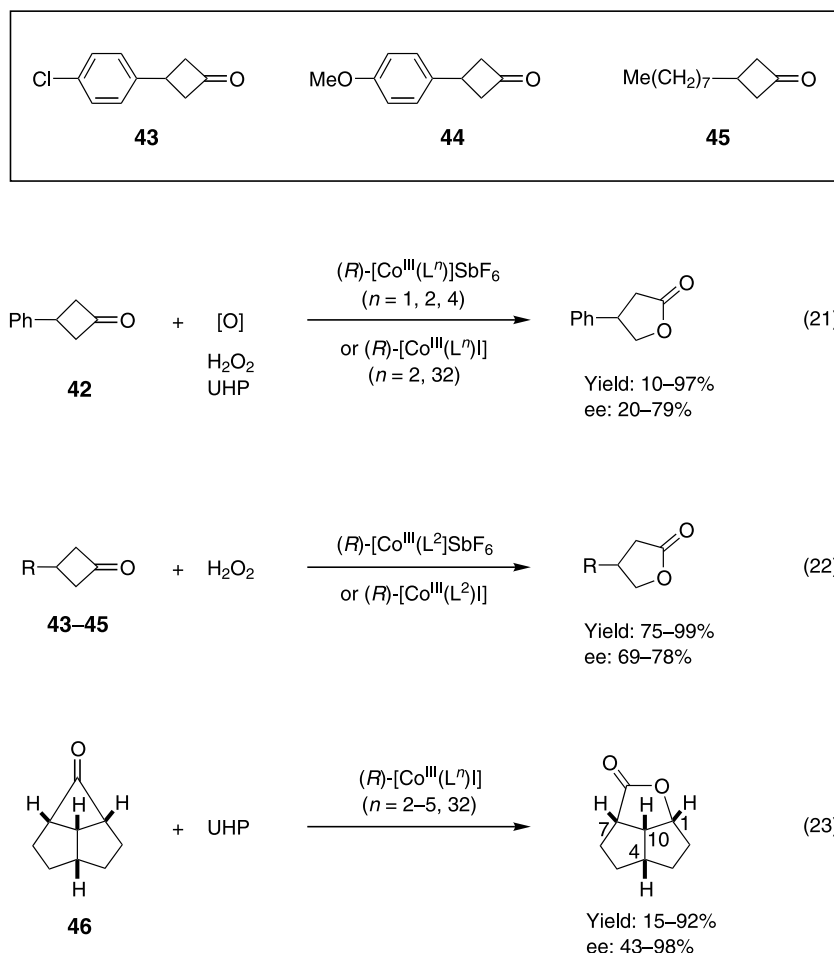
Katsuki and co-workers also found that $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^2)]\text{SbF}_6$ and $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^2)]\text{I}$ can catalyze Baeyer-Villiger oxidations of other cyclobutanone derivatives **43–45** as well, affording the corresponding lactones in 75–99% yields and 69–78% ee by employing H_2O_2 as an oxidant (reactions (22) in **Scheme 10**) [25]. However, extension of reaction (22) to tricyclo[4.2.1.0^{3,9}]nonan-2-one (**46**) results in lower enantioselectivity (36% ee for $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^2)]\text{I}$). Interestingly, changing the oxidant from H_2O_2 to UHP and replacing catalyst $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^2)]\text{I}$ with $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^n)]\text{I}$ ($n = 3\text{--}5, 32$) markedly enhance the enantiocontrol for the Baeyer-Villiger oxidation of **46** (reaction (23) in **Scheme 10**). The best catalyst among $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^n)]\text{I}$ ($n = 2\text{--}5, 32$) for reaction (23) is $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^{32})]\text{I}$, which leads to formation of the desired lactone product in 92% yield and 98% ee [25].

5.8. Diels-Alder reactions of 1,2-dihydropyridine

Diels-Alder reactions of protected 1,2-dihydropyridines serve as a well-established route to 2-azabicyclo[2.2.2]octane skeleton, a structural unit widely observed in natural products such as alkaloids [27]. By employing chromium complexes of binaphthyl Schiff-base ligands as catalysts, Rawal and co-workers recently realized a catalytic enantioselective Diels-Alder reactions of a protected 1,2-dihydropyridine [27]. They demonstrated that reactions of 1-phenoxy carbonyl-1,2-dihydropyridine with *N*-acryloyloxazolidinone (**47**) in the presence of catalysts $(R)\text{-}$ or $(S)\text{-}[\text{Cr}^{\text{III}}(\text{L}^n)]\text{X}$ ($n = 3, 6, 23, 24, 27, 28$; $\text{X} = \text{BF}_4, \text{SbF}_6, \text{OTf}$) selectively afford the corresponding *endo*-cycloadduct in 61–99% yields



Scheme 8.



Scheme 10.

and 23–85% ee (reactions (24) and (25) in Scheme 11). The reactions give best results by using acetone as a solvent; in this solvent the *endo*-cycloadduct can be formed in 86–99% yield and 70–85% ee except for catalyst (*S*)-[Cr^{III}(L²⁷)]OTf. The highest enantioselectivity (85% ee), coupled with an excellent product yield of 99%, is observed for reaction (25) catalyzed by (*R*)-[Cr^{III}(L⁶)]SbF₆.

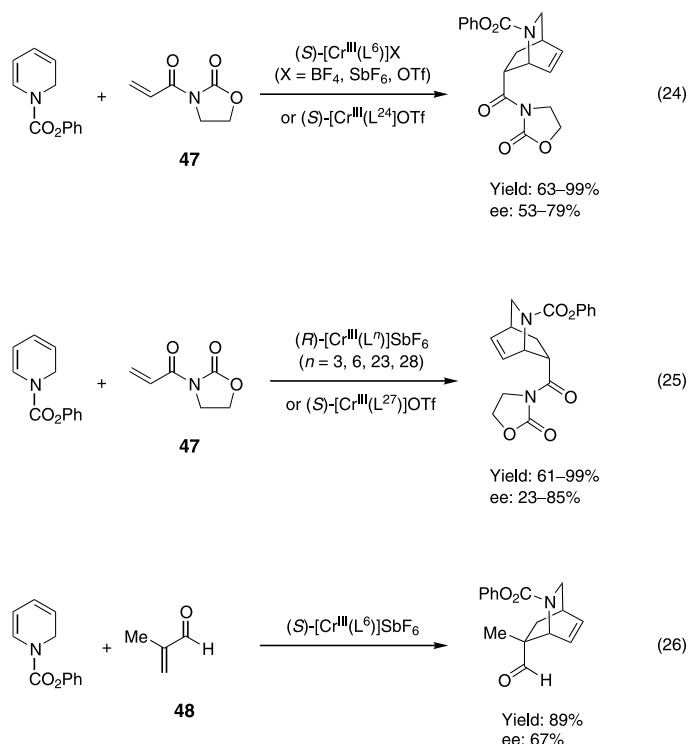
The foregoing [Cr^{III}(Lⁿ)]X-catalyzed Diels-Alder reactions of protected 1,2-dihydropyridine are extendable to methacrolein (**48**), which contains a substituent at the α -position. Reaction of 1-phenoxycarbonyl-1,2-dihydropyridine with **48** in the presence of catalyst (*S*)-[Cr^{III}(L⁶)]SbF₆ gives the respective *endo*-cycloadduct in 89% yield and 67% ee (reaction (26) in Scheme 11) [27]. Such an enantioselectivity is much higher than that (ca. 10% ee) achieved for the same reaction catalyzed by the 1,2-cyclohexyl analogue of (*S*)-[Cr^{III}(L⁶)]SbF₆ [27].

5.9. Ring-opening polymerization of lactide

In 1996, Spassky and co-workers reported that complex (*R*)-[Al^{III}(L¹)(OMe)] effects kinetic resolution

of *rac*-lactide (**49**) to form an isotactic poly(acetic acid) in 88% ee at 20% conversion [40] (reaction (27) in Scheme 12). Three years later, Coates and Ovitt found that complex (*R*)-[Al^{III}(L¹)(O^{*i*}Pr)] catalyzes ring-opening polymerization of *meso*-lactide (**50**) in a stereoselective manner, affording a highly syndiotactic poly(acetic acid) with a 94% conversion [15] (reaction (28) in Scheme 12). The enantiotopic selectivity in the (*R*)-[Al^{III}(L¹)(O^{*i*}Pr)]-catalyzed polymerization was calculated to be 96%. This provides a new method for constructing syndiotactic polymers, that is by stereoselective ring-opening polymerization of a cyclic monomer containing two stereocenters [15].

Shortly after the work by Coates et al., Radano et al. reported stereoselective polymerization of *rac*-**49** with *rac*-[Al^{III}(L¹)(O^{*i*}Pr)] to form a polylactide stereocomplex [17] as depicted in reaction (29) of Scheme 12. This process provides a direct access to poly(acetic acid) stereocomplex from a racemic lactide, unlike previous route to such stereocomplexes (which requires preparation of enantiopure (*R*)- and (*S*)-poly(acetic acid) and subsequent combination of the chiral polylactide chains).



Scheme 11.

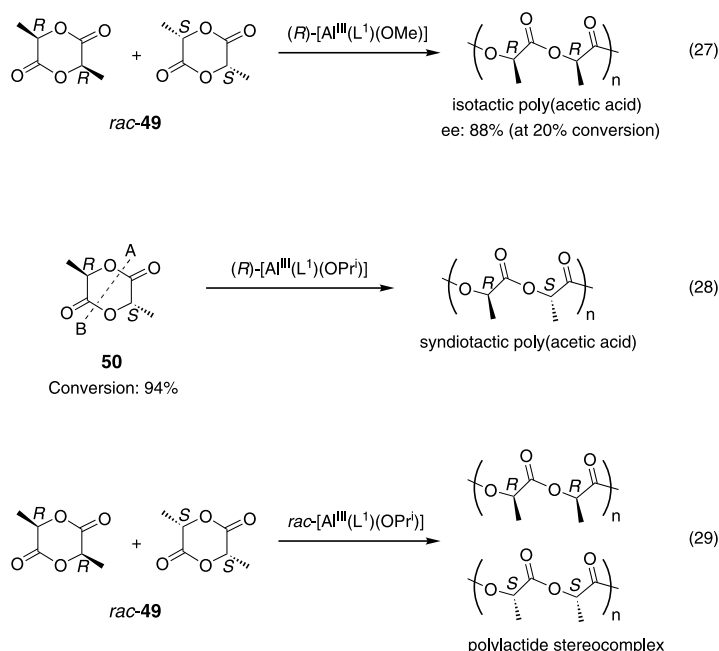
Recent work by Coates and Ovitt provides a more detailed study on the stereoselective polymerization of **50** catalyzed by (R) -[Al^{III}(L¹)(OⁱPr)] [23]. They found that this chiral catalyst opens the *meso*-lactide preferentially at site B (see Scheme 12). When (R) -[Al^{III}(L¹)(OⁱPr)] rather than (R) -[Al^{III}(L¹)(OⁱPr)] is used as a catalyst, the polymerization of **50** affords a

heterotactic poly(acetic acid). Polymerization of rac -**49** with rac -[Al^{III}(L¹)(OⁱPr)] has also been examined, which gives an isotactic stereoblock poly(acetic acid). Based on the absolute stereochemistry of ring-opening of **50** with (R) -[Al^{III}(L¹)(OⁱPr)], Coates and Ovitt proposed a mechanism for each of the processes that lead to formation of the foregoing syndiotactic, heterotactic, and stereoblock poly(acetic acid) [23].

6. Summary

(i) Reactions of enantiomerically pure 2-amino-2'-R-1,1'-binaphthyl (R = NH₂ or OH) and salicylaldehyde derivatives give a variety of chiral binaphthyl Schiff-base ligands H₂Lⁿ or Lⁿ, ranging from tetradentate N₂O₂ ligands H₂L^{1–33} to bidentate ligands L^{34–39}, and to tridentate ligands H₂L^{40–46}. Similar treatments of partially hydrogenated 2,2'-diamino-1,1'-binaphthyl with salicylaldehyde derivatives afford chiral tetradentate N₂O₂ ligands H₂L^{47–49}.

(ii) Reactions of H₂Lⁿ with metal compounds give chiral complexes [M^{II}(Lⁿ)] (M = Mn, Fe, Co, Ni, Cu, Zn, Pd), [M^{III}(Lⁿ)X] (M = Al, Cr, Mn, Fe, Co, Y), [M^{III}(Lⁿ)X] (M = Al, Cr, Co), [M^{IV}(Lⁿ)(OR)₂] (M = Ti, Zr), [Ru^{II}(Lⁿ)(NO)Cl], [Cu^{II}(HLⁿ)₂], [Cu^{II}(Lⁿ)₂], and [M^{III}(Lⁿ)₂(OMe)₂] (M = Al, Mn). The structures of rac -[Cu^{II}(Lⁿ)] ($n = 1, 3, 26$), (S) -[Cu^{II}(L⁴)], rac -[M^{III}(L³)(acac)] (M = Mn, Fe), (S) -[Ru^{II}(L³)(NO)Cl], rac -[Al^{III}(L⁶)(H₂O)₂]OTf, rac -[Al^{III}(L⁶)Cl], rac -[Co^{II}(L³)(H₂O)], (R) -[Y^{III}(L¹)(OCH₂CH₂NMe₂)], (R,R) -[Al^{III}(L¹)₂(OMe)₂], rac -[Pd^{II}(L³)], (R) -[Pd^{II}(L⁴⁸)], (R) -[Co^{II}(L³)(DMSO)₂], (S,S) -[Cu^{II}(HL⁴³)₂], and (R,S) -



Scheme 12.

$[\text{Cu}_2^{\text{II}}(\text{L}^{43})_2]$ have been determined by X-ray crystallography. In almost all the cases, the tetradentate binaphthyl Schiff-base ligands $[\text{L}^n]^{2-}$ ($n = 1, 3, 4, 6, 26$) adopt a non-planar N_2O_2 coordination mode, unlike the basically planar N_2O_2 geometry usually observed for salens.

(iii) Complexes $(R)\text{-}[\text{Al}^{\text{III}}(\text{L}^1)(\text{OR})]$ ($R = \text{Me}, i\text{-Pr}$) and $rac\text{-}[\text{Al}^{\text{III}}(\text{L}^1)(\text{O}^i\text{Pr})]$ efficiently catalyze stereoselective ring-opening polymerization of lactide, including kinetic resolution of *rac*-lactide, formation of syndiotactic polymers from *meso*-lactide, and formation of polylactide stereocomplex from *rac*-lactide.

(iv) The following complexes give moderate to good enantioselectivity in catalyzing organic transformations: $(R)\text{-}[\text{Co}^{\text{II}}(\text{L}^1)]$ for hydroxylation of styrene, $(S)\text{-}[\text{Mn}^{\text{II}}(\text{L}^n)]$ ($n = 1, 3, 4$), $(R)\text{-}[\text{Mn}^{\text{III}}(\text{L}^n)(\text{OAc})]$ ($n = 3, 30$), $(R)\text{-}[\text{Mn}^{\text{III}}(\text{L}^3)(\text{acac})]$, $(R)\text{-}[\text{Pd}^{\text{II}}(\text{L}^{48})]$, and $(R)\text{-}[\text{Cr}^{\text{III}}(\text{L}^4)\text{Cl}]\text{-MCM-41(m)}$ for alkene epoxidation, $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^n)]$ ($n = 3\text{--}5, 9\text{--}11, 16, 18, 25, 30$) for alkene cyclopropanation, $(S)\text{-}[\text{Cu}^{\text{II}}(\text{L}^6)]$ for desymmetrization of *meso*-*N*-sulfonylaziridine, $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^n)]\text{SbF}_6$ ($n = 1, 2, 4$) or $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^n)]\text{I}$ ($n = 2\text{--}5, 32$) for Baeyer-Villiger oxidation of aryl cyclobutanone, and $(R)\text{-}$ or $(S)\text{-}[\text{Cr}^{\text{III}}(\text{L}^n)]\text{X}$ ($n = 3, 6, 23, 28$; $\text{X} = \text{BF}_4, \text{SbF}_6, \text{OTf}$) for Diels-Alder reactions of 1,2-dihydropyridine. Some of these complexes exhibit significantly higher enantiocontrol than their salen analogues.

(v) The following complexes are excellent catalysts for stereoselective organic transformations: $(R)\text{-}[\text{Ti}^{\text{IV}}(\text{L}^{40})(\text{O}^i\text{Pr})_2]$ and $(R)\text{-}[\text{Ti}^{\text{IV}}(\text{L}^{40})(\text{DTBSA})]$ for aldol addition reactions, $(R)\text{-}[\text{Al}^{\text{III}}(\text{L}^6)(\text{H}_2\text{O})_2]\text{OTf}$ and $(R)\text{-}[\text{Al}^{\text{III}}(\text{L}^6)]\text{SbF}_6$ for aldol addition/acyl transfer reactions, titanium complexes formed in situ from $\text{Ti}(\text{O}^i\text{Pr})_4 + (R)\text{-}$ or $(S)\text{-H}_2\text{L}^6$ for trimethylsilylcyanation of aldehydes, copper complexes formed in situ from $(R)\text{-L}^{38} + \text{CuOTf}$ or $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ for cyclopropanation of diaryl substituted terminal alkenes with *l*-menthyl diazoacetate, and $(R)\text{-}[\text{Co}^{\text{III}}(\text{L}^{32})\text{I}]$ for Baeyer-Villiger oxidation of tricyclic cyclobutanone. By employing these catalysts, the desired organic products can be obtained in $>90\%$ ee.

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