Copper Complexes of Chiral Tetradentate Binaphthyl Schiff-Base Ligands: Syntheses, X-ray Crystal Structures and Activity in Catalytic Asymmetric Cyclopropanation of Alkenes

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Keywords: Asymmetric catalysis / Copper / Cyclopropanation / Schiff bases / Structure elucidation

A number of new chiral monomeric binaphthyl Schiff-base ligands H_2L [where H_2L = 2,2′-bis(3-R^1-5-R^2-2-hydroxybenzylideneamino)-1,1′-binaphthyl] and a series of chiral copper(II) complexes [CuL] were prepared in good or nearly quantitative yields. Some of the free ligands and the [CuL] complexes were structurally characterized by X-ray crystallography. Almost all the [CuL] complexes were found to be active catalysts for the asymmetric cyclopropanation of alkenes with ethyl or *tert*-butyl diazoacetate. Enantioselectivities of up to 77% *ee* were observed.

Introduction

Optically active cyclopropanes play an important role as intermediates in the syntheses of insecticides and drugs.[1] In this context, the search for effective catalysts for asymmetric cyclopropanation has continued to attract considerable interest.[2−3] Chiral ligands such as semicorrine,[4−7] bisoxazolines,[8−12] bipyridines[13−19] and Schiff bases[20−23] are the most efficient ligands for copper-catalyzed alkene cyclopropanation with diazoacetate.

Schiff-base ligands bearing a C_2-chiral auxiliary have been employed for a number of metal-catalyzed asymmetric reactions, such as Cu-catalyzed aziridination,[24−25] Mn-catalyzed epoxidation,[26] Co-catalyzed cyclopropanation,[27−29] Cr-catalyzed ring opening[30] and the hetero-Diels−Alder reaction.[31] In view of the excellent enantiofacial discriminating power exhibited by binaphthylic ligands in asymmetric metal catalysis,[32] we have previously studied the binaphthylic Schiff-base ligands 2,2′-bis(3-R^1-5-R^2-2-hydroxybenzylideneamino)-1,1′-binaphthyl (H_2L) and reported the use of their manganese and chromium complexes in the asymmetric oxidation of alkenes[33−35] and their titanium complexes in the asymmetric trimethylsilylcyanation of aldehydes.[36] Recently, great interest in the copper complexes of these binaphthylic Schiff-base ligands has arisen from a study of their derivatives as models for catalytic galactose oxidase.[37]

In the present work we describe the synthesis of a series of chiral copper(II)-binaphthyl Schiff-base complexes [CuL] together with several new chiral H_2L ligands. Some of the H_2L and [CuL] compounds were characterized by X-ray crystallography. The use of [CuL] complexes as catalysts for the asymmetric cyclopropanation of alkenes with an alkyl diazoacetate was explored, and this represents the first asymmetric alkene cyclopropanation catalyzed by metal complexes bearing a tetradentate binaphthyl Schiff-base ligand.

Results and Discussion

Synthesis of Chiral Schiff-base Ligands H_2L and Their Copper(II) Complexes [CuL]

Treatment of chiral 2,2′-diamino-1,1′-binaphthyl with various substituted salicylaldehydes afforded a series of chiral binaphthyl Schiff-base ligands H_2L^{1-13} in good yields. The preparation and characterization of $H_2L^{1,2,4-9}$ have been reported previously by us.[33,35] The new ligands $H_2L^{3,10-13}$ described in this work were obtained as orange crystalline solids and were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy (see Exp. Sect.). The key NMR spectral features of $H_2L^{3,10-13}$ include the imine proton resonances at δ = 8.53−8.73 (singlets), the aromatic proton resonances at δ = 6.62−8.15 (multiplets), the phenolic proton resonances at δ = 12.06−13.46 (broad singlets), and the

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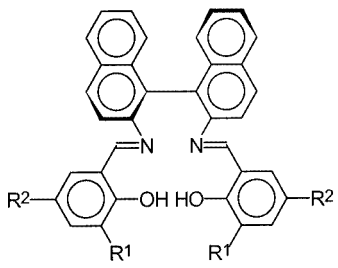
^{13}C resonances of the CH=N groups at $\delta = 160.3-163.3$ (singlets), all of which are similar to those reported for $H_2L^{1,2,4-9}$.[33,35] The IR spectra of $H_2L^{3,10-13}$ each show a strong band in the 3075−3800 cm^{-1} region attributable to ν(OH) and a band at about 1613 cm^{-1} attributable to ν(C=N).



Ligand	R^1	R^2
H_2L^1	Cl	Cl
H_2L^2	Br	Br
H_2L^3	I	I
H_2L^4	*t*Bu	*t*Bu
H_2L^5	Cl	*t*Bu
H_2L^6	*t*Bu	Cl
H_2L^7	*t*Bu	NO_2
H_2L^8	Et	NO_2
H_2L^9	H	NO_2
H_2L^{10}	H	Cl
H_2L^{11}	Cl	H
H_2L^{12}	EtO	H
H_2L^{13}	H	Ph

The chiral copper complexes of H_2L^{1-13} were prepared from the reaction of optically active H_2L^{1-13} with $Cu(OAc)_2$ in dichloromethane/methanol at room temperature. These complexes are air stable both as solids and in solution, as revealed by visible or IR spectroscopy. Elemental analysis indicated that they have a Cu:L molar ratio of 1:1. A principal feature of the IR spectra of these complexes is the intense absorption band ranging from 1584 to 1619 cm^{-1} which is assigned to ν(C=N). These ν(C=N) bands are shifted by about 10−27 cm^{-1} from those of the corresponding H_2L^{1-13} ligands.

X-ray Structure Analyses

The structures of H_2L^{12} and $[CuL^2]$ were determined by X-ray crystallography (see Figure 1−2). The crystallographic data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2−3.

Previously we reported the X-ray crystal structure of the racemic form of complex $[CuL^1]$.[33] Like $[CuL^1]$, the complex $[CuL^2]$ features a distorted tetrahedral CuN_2O_2 core. The bond angles in the CuN_2O_2 core lie in the range 88.7°−154.0° ($[CuL^2]$). The Cu−N and Cu−O bond lengths are ≈1.97 and ≈1.90 Å, respectively. CuL^2 also possesses a twisted seven-membered CuN_2C_4 ring. The dihedral angle between the two naphthyl rings is 72.49°, which is similar to that in $[CuL^1]$ (≈75°) but is considerably smaller than that of the free H_2L^{12} ligand (85.54°). Comparison of the structures of $[CuL^{1,2}]$ with the reported X-ray structure of a copper complex of the chiral Schiff base with a cyclohexyl rather than a binaphthyl moiety clearly shows that the binaphthyl moieties of $[CuL^{1,2}]$ enforce a non-square planar coordination geometry, while the cyclohexyl moiety prefers a square planar environment.

Enantioselective Cyclopropanation of Alkenes Catalyzed by CuL

Having prepared the copper complexes $[CuL^{1-13}]$, we studied their catalytic activities towards the asymmetric cyclopropanation of styrene with alkyl diazoacetates N_2CHCO_2R (R = Et, *t*Bu). The results are compiled in Table 4. Note that all the reactions were carried out in styrene. To reduce the formation of side products such as fumarate and maleate, the alkyl diazoacetate was added slowly in each case.

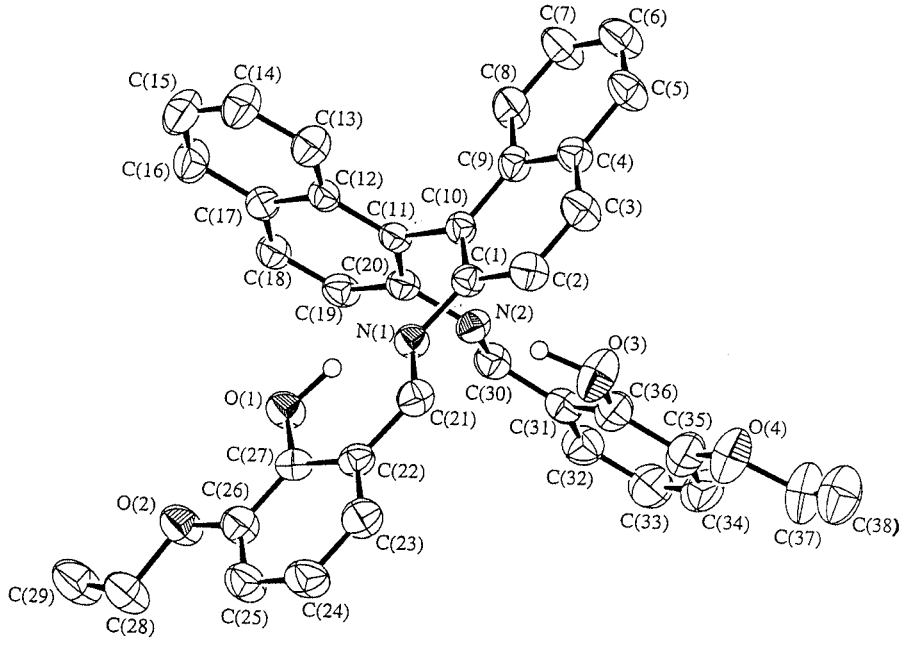


Figure 1. ORTEP drawing of H_2L^{12}

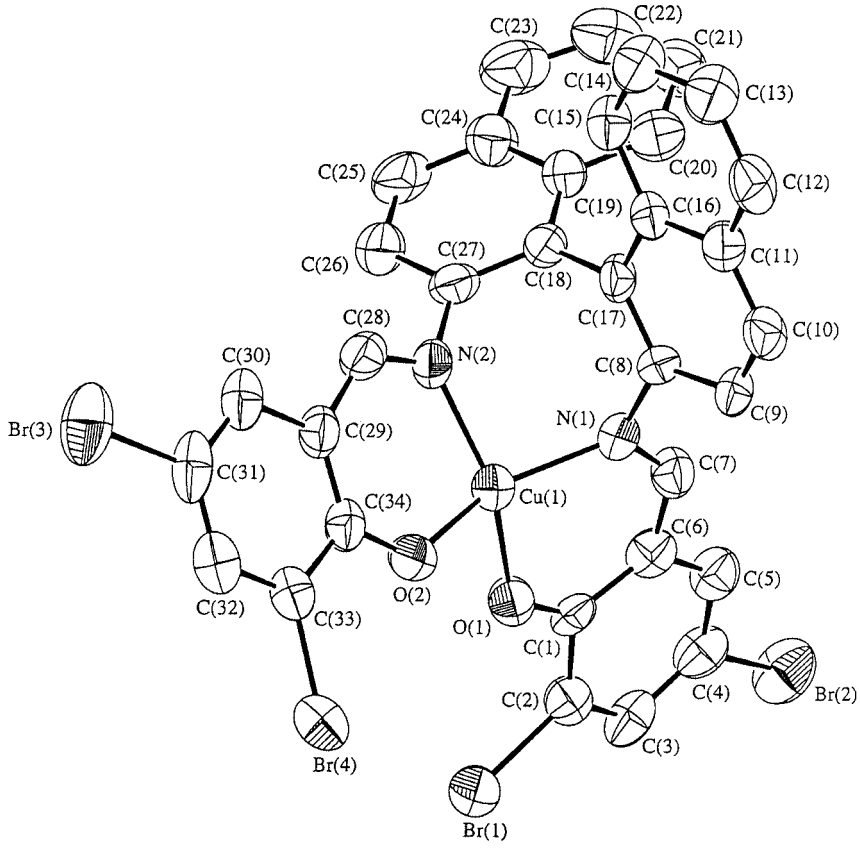


Figure 2. ORTEP drawing of [CuL^2]

Table 1. Crystallographic data for H_2L^{12} and [CuL^2]

	H_2L^{12}	[CuL^2]
Formula	$C_{38}H_{32}N_2O_4{\cdot}CH_2Cl_2$	$C_{34}H_{18}N_2O_2Br_4Cu{\cdot}2CH_2Cl_2$
F_w	665.61	1039.56
Color	orange	brown
Crystal system	triclinic	monoclinic
Space group	*P*1	*C*2/*c*
a [Å]	11.657(2)	36.453(3)
b [Å]	12.124(2)	12.581(2)
c [Å]	13.788(2)	17.039(3)
V [Å^3]	1652.3(6)	7600(1)
Z	2	8
Crystal dimensions [mm^3]	0.25 × 0.10 × 0.35	0.20 × 0.15 × 0.30
F(000)	696	4040
Radiation [Å]	0.7107	0.7107
hkl range *h*:	0 → 14	0 → 43
k	−12 → 14	0 → 14
l	−15 → 16	−19 → 14
Reflections collected (unique)	5164	6208
Obs. Reflections [$I > 3\sigma(I)$]	3295	3318
No. of variables	430	442
$2\theta_{max}$ [°]	51.1	51.0
(D-map) max. min. [e Å^{-3}]	0.48; 0.54	1.00; 0.89
R	0.070	0.055
R_w	0.108	0.066

Table 2. Selected bond lengths [Å] and angles [°] for H_2L^{12}

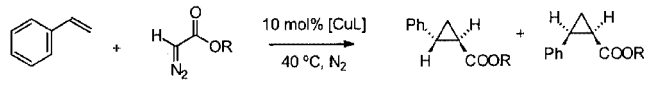
Bond lengths			
C(10)−C(l 1)	1.508(5)	O(1)−C(27)	1.347(5)
O(2)−C(26)	1.382(5)	O(2)−C(28)	1.447(5)
O(3)−C(36)	1.351(5)	O(4)−C(35)	1.371(6)
O(4)−C(37)	1.405(7)	N(1)−C(1)	1.411(5)
N(1)−C(21)	1.291(5)	N(2)−C(20)	1.414(5)
N(2)−C(30)	1.281(5)	C(21)−C(22)	1.437(6)
C(30)−C(31)	1.457(6)	C(28)−C(29)	1.517(7)
C(37)−C(38)	1.424(8)		
Bond angles			
C(26)−O(2)−C(28)	116.8(4)	C(35)−O(4)−C(37)	118.1(5)
C(1)−N(1)−C(21)	122.5(3)	C(20)−N(2)−C(30)	122.1(3)
N(l)−C(1)−C(2)	124.3(3)	N(1)−C(1)−C(10)	116.6(3)
N(2)−C(20)−C(11)	116.9(3)	N(2)−C(20)−C(19)	123.1(3)
N(l)−C(21)−C(22)	121.9(4)	N(2)−C(30)−C(31)	121.0(4)
O(2)−C(26)−C(25)	124.4(4)	O(2)−C(26)−C(27)	115.4(4)
O(1)−C(27)−C(22)	122.1(4)	O(1)−C(27)−C(26)	118.3(4)
O(2)−C(28)−C(29)	105.8(4)	O(4)−C(35)−C(34)	127.1(5)
O(4)−C(35)−C(36)	113.8(4)	O(3)−C(36)−C(31)	121.6(4)
O(3)−C(36)−C(35)	118.9(4)	O(4)−C(37)−C(38)	111.5(6)

Table 3. Selected bond lengths [Å] and angles [°] for $[CuL^2]$

Bond lengths			
Br(1)−C(2)	1.879(9)	Cu(1)−N(2)	1.912(7)
Br(2)−C(4)	1.906(9)	O(1)−C(1)	1.296(9)
Br(3)−C(31)	1.890(l)	O(2)−C(34)	1.306(9)
Br(4)−C(33)	1.881(l0)	N(1)−C(7)	1.290(l)
Cu(1)−O(1)	1.899(6)	N(1)−C(8)	1.440(l)
Cu(1)−O(2)	1.907(6)	N(2)−C(27)	1.430(l)
Cu(1)−N(1)	1.963(7)	N(2)−C(28)	1.290(l)
Bond angles			
O(1)−Cu(1)−O(2)	88.8(3)	Cu(1)−N(2)−C(27)	118.9(6)
O(1)−Cu(1)−N(1)	92.3(3)	Cu(1)−N(2)−C(28)	123.2(7)
O(1)−Cu(1)−N(2)	154.0(3)	C(27)−N(2)−C(28)	116.9(8)
O(2)−Cu(1)−N(1)	151.3(3)	Br(1)−C(2)−C(1)	117.6(7)
O(2)−Cu(1)−N(2)	94.2(3)	Br(1)−C(2)−C(3)	120.1(8)
N(1)−Cu(1)−N(2)	97.2(3)	Br(2)−C(4)−C(3)	120.3(8)
Cu(1)−O(1)−C(l)	127.0(6)	Br(2)−C(4)−C(5)	118.3(8)
Cu(1)−O(2)−C(34)	127.8(6)	Br(3)−C(31)−C(30)	118.0(10)
Cu(1)−N(1)−C(7)	124.3(7)	Br(3)−C(31)−C(32)	121.9(9)
Cu(1)−N(1)−C(8)	115.5(5)	Br(4)−C(33)−C(32)	119.3(8)
C(7)−N(1)−C(8)	119.2(8)	Br(4)−C(33)−C(34)	119.6(7)

The results in Table 4 reveal that complexes $[CuL^{1-3,5,8-13}]$ are active catalysts for the above styrene cyclopropanations. The yields of the isolated cyclopropyl esters were moderate to excellent (32−99%) and the enantioselectivities obtained range from 3 to 73% *ee*. GLC analysis of the reaction mixtures showed that the *trans*/*cis* ratios of the cyclopropyl esters fall in the range of 65:35 to 80:20. The absolute configurations of the cyclopropyl esters were determined to be (*1S,2S*) and (*1S,2R*) for the *trans*- and *cis*-isomers, respectively. Variation of the structure of the

Table 4. Catalytic asymmetric cyclopropanation of styrene with chiral [CuL] complexes



Entry[a]	Catalyst	R	*trans*:*cis*	% *ee* (*trans*)[b]	% *ee* (*cis*)[b]	% Yield[c]
1	$[CuL^1]$	Et	73:27	10 (1*S*,2*S*)	13 (1*S*,2*R*)	42
2		*t*Bu	75:25	35 (1*S*,2*S*)	48 (1*S*,2*R*)	48
3	$[CuL^2]$	Et	66:34	16 (1*S*,2*S*)	28 (1*S*,2*R*)	77
4		*t*Bu	73:27	47 (1*S*,2*S*)	66 (1*S*,2*R*)	80
5	$[CuL^3]$	Et	72:28	8 (1*S*,2*S*)	19 (1*S*,2*R*)	42
6		*t*Bu	71:29	33 (1*S*,2*S*)	56 (1*S*,2*R*)	73
7	$[CuL^4]$	Et	−	−	−	n.d.
8		*t*Bu	−	−	−	n.d.
9	$[CuL^5]$	Et	68:32	6 (1*S*,2*S*)	22 (1*S*,2*R*)	44
10		*t*Bu	75:25	10 (1*S*,2*S*)	40 (1*S*,2*R*)	39
11	$[CuL^6]$	Et	−	−	−	n.d.
12		*t*Bu	−	−	−	n.d.
13	$[CuL^7]$	Et	−	−	−	n.d.
14		*t*Bu	−	−	−	n.d.
15	$[CuL^8]$	Et	79:21	1 (1*S*,2*S*)	3 (1*S*,2*R*)	32
16		*t*Bu	80:20	22 (1*S*,2*S*)	43 (1*S*,2*R*)	57
17	$[CuL^9]$	Et	66:34	2 (1*S*,2*S*)	3 (1*S*,2*R*)	55
18		*t*Bu	69:31	15 (1*S*,2*S*)	38 (1*S*,2*R*)	44
19	$[CuL^{10}]$	Et	70:30	3 (1*S*,2*S*)	4 (1*S*,2*R*)	53
20		*t*Bu	74:26	14 (1*S*,2*S*)	35 (1*S*,2*R*)	82
21	$[CuL^{11}]$	Et	65:35	11 (1*S*,2*S*)	18 (1*S*,2*R*)	60
22		*t*Bu	77:23	74 (1*S*,2*S*)	73 (1*S*,2*R*)	83
23	$[CuL^{12}]$	Et	73:27	12 (1*S*,2*S*)	12 (1*S*,2*R*)	52
24		*t*Bu	76:24	26 (1*S*,2*S*)	31 (1*S*,2*R*)	66
25	$[CuL^{13}]$	Et	70:30	12 (1*S*,2*S*)	19 (1*S*,2*R*)	71
26		*t*Bu	74:26	14 (1*S*,2*S*)	35 (1*S*,2*R*)	99

[a] Styrene was used as solvent. [b] For R = Et, enantiomeric excesses were determined by HPLC with Daicel Chiralcel OJ column. For R = *t*Bu, enantiomeric excesses were determined by GC with a chiraldex β-PH column. Absolute configurations were determined by comparing the order of elution of samples with known configuration (ref.[4]). [c] Isolated yield after chromatography.

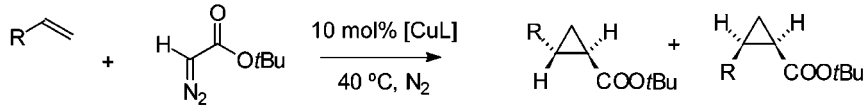
diazoacetates had a large effect on both *trans*/*cis* diastereoselectivity and enantioselectivity. As shown in Table 4, when the R group changes from ethyl to a bulkier *tert*-butyl group the reactions gave higher *trans*/*cis* ratios and *ee*'s. This is consistent with the trend previously observed for other copper catalysts.[4] To the best of our knowledge, complexes $[CuL^{1-3,5,8-13}]$ are the first examples of a well-defined tetrahedral copper complex that is active for alkene cyclopropanation.

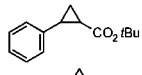
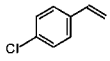
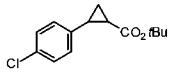
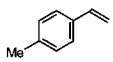
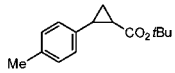
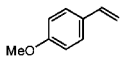
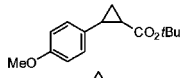
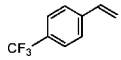
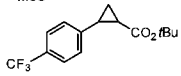
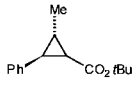
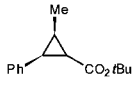
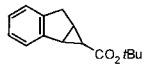
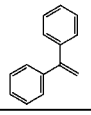
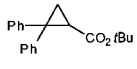
We found that ligands with different substituents on the phenolic rings of the Schiff-base ligands gave different results in both reactivity and selectivity, similar to the observation reported by Jacobsen and co-workers in the Mn-catalyzed epoxidation of alkenes.[38] For example, $[CuL^2]$, with $R^1 = R^2 = Br$ (entries 3 and 4), gave a higher enantioselectivity than $[CuL^{1,3}]$, with $R^1 = R^2 = Cl$ (entries 1 and 2), or I (entries 5−6). The effect of R^1 groups on the catalyst activity can be evaluated by comparing the results obtained for $[CuL^{1,6,10}]$ ($R^2 = Cl$; $R^1 = Cl$, *t*Bu and H respectively; see entries 1, 2, 11, 12, 19, and 20), and for $[CuL^{7-9}]$ ($R^2 =$

NO_2; R^1 = *t*Bu, Et and H, respectively, see entries 13−18), which shows that ligands with either electron-withdrawing or electron-donating R^1 groups (such as Cl or Et) *increased* the enantioselectivity. However, the ligands with R^1 = *t*Bu form the complexes [$CuL^{4,6,7}$] that are inactive in cyclopropanation (entries 7, 8, 11−14). This might be due to the bulkiness of the *t*Bu groups, which prevents the copper centers from interacting effectively with the incoming diazoacetates or styrene. The effect of R^2 groups on the catalyst activity is different from that of the R^1 groups. Comparison of the results obtained for [$CuL^{1,5,11}$] (R^1 = Cl; R^2 = Cl, *t*Bu and H, respectively; see entries 1, 2, 9, 10, 21, and 22), and for [$CuL^{9,10,13}$] (R^1 = H; R^2 = NO_2, Cl and Ph, respectively; see entries 17−20, 25 and 26) reveals that ligands with either electron-withdrawing or electron-donating R^2 groups almost all *reduced* the enantioselectivity. Also, the catalyst with R^2 = *t*Bu groups is active in cyclopropanation (entries 9 and 10). These results demonstrate that the reactivity and selectivity of the [CuL^{1-13}]-catalyzed styrene cyclopropanations are greatly affected by both the steric and electronic properties of the R^1 groups and by the electronic properties of the R^2 groups in the catalysts.

Evidently, of the thirteen copper complexes [CuL^{1-13}], complexes [$CuL^{2,11}$] are the best catalysts for the styrene cyclopropanation in terms of the product yields and enantioselectivity (see Table 4). Therefore, we studied the cyclopropanation of other alkenes with these two catalysts. The reactions were carried out in dichloromethane instead of styrene in order to get a better comparison of the substrate effects. Table 5 shows the results obtained for the cyclopropanation of various alkenes with *tert*-butyl diazoacetate. The isolated yields of cyclopropyl esters were good to excellent (57−96%) and the *trans*/*cis* ratios ranged from 74:26 to 90:10. Comparison of entries 1 and 2 in Table 5 with entries 4 and 22 in Table 4 indicates that the *trans*/*cis* ratios obtained in dichloromethane are higher than in styrene, although lower enantioselectivities were attained in the former solvent. For the cyclopropanation of most of the al-

Table 5. Catalytic asymmetric cyclopropanation of alkenes with chiral [CuL] complexes



Entry	Catalyst	Substrate	Product	*trans*:*cis*	% ee (*trans*)[b]	% ee (*cis*)[b]	Yield %[c]
1	[CuL^2]			78:22	56 (*1S,2S*)	52 (*1S,2R*)	80
2	[CuL^{11}]			81:19	61 (*1S,2S*)	48 (*1S,2R*)	57
3	[CuL^2]			76:24	54	51	84
4	[CuL^{11}]			85:15	77	66	89
5	[CuL^{11}]			80:20	67	56	89
6	[CuL^{11}]			75:25	61	56	65
7	[CuL^{11}]			76:24	60	62	83
8	[CuL^2]			85:15	44	32	82
9	[CuL^{11}]			90:10	55	29	57
10	[CuL^2]			74:26	37	48	62
11	[CuL^{11}]			81:19	63	44	63
12	[CuL^2]			79:21	50	41	70
13	[CuL^{11}]			80:20	17	22	96
14	[CuL^2]			–	50		89
15	[CuL^{11}]			–	62		90

[a] Dichloromethane was used as solvent. [b] For entries 1−7 and 12−15, enantiomeric excesses were determined by GC with a chiraldex β-PH column. For entries 8−11, enantiomeric excesses were determined by literature procedure (ref.[4]). Absolute configurations were determined by comparing the order of elution of samples with known configuration (ref.[4]). [c] Isolated yield after chromatography.

kenes in Table 5, [CuL[11]] was a better catalyst than [CuL[2]]. The former catalyst gave 77 and 66% *ee* (*trans*- and *cis*-isomers, respectively) for the cyclopropanation of chlorostyrene (entry 4) and a 90:10 *trans*/*cis* ratio for the cyclopropanation of *trans*-β-methylstyrene (entry 9), which are the highest *ee* value or *trans*/*cis* ratio in Table 5.

To probe the nature of the active intermediates in the cyclopropanation reactions, we measured the relative rates of the [CuL[2]]-catalyzed cyclopropanation of substituted styrenes with EDA through competition experiments. The Hammett plot of $\log(K_X/K_H)$ versus σ^+ is shown in Figure 3, which indicates that substituted styrenes with electron-donating groups (such as 4-methoxy- and 4-methylstyrenes) gave larger cyclopropanation rates, whereas those with electron-withdrawing groups (such as 4-chloro- and 4-trifluoromethylstyrenes) gave smaller cyclopropanation rates. A good σ^+ correlation is obtained with $\rho = -0.72$. This value is similar to those of other copper catalysts such as copper-terpyridine ($\rho = -0.79$) and copper-di-pyridyl ketone ($\rho = -0.74$) recently reported by our group.[39,40] The small negative value of ρ obtained supports the formation of electrophilic metal−carbene intermediates and only a moderate positive charge build-up at the benzylic carbon in the transition state in both systems.

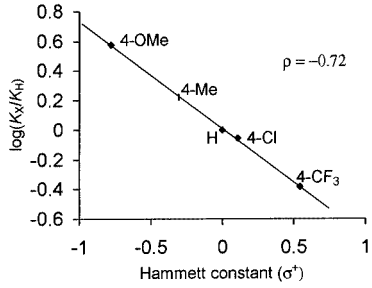


Figure 3. Hammett plot for the [CuL[2]]-catalyzed cyclopropanation of styrene with EDA

Conclusion

We have synthesizeds a series of tetrahedral copper(II) Schiff-base complexes [CuL] in nearly quantitative yield from the reaction of $Cu(OAc)_2$ with the chiral tetradentate binaphthyl Schiff-base ligands 2,2′-bis(3-R^1-5-R^2-2-hydroxybenzylideneamino)-1,1′-binaphthyl (H_2L). The structures of [CuL] feature distorted tetrahedral CuN_2O_2 cores, as revealed by X-ray crystallography. Almost all the chiral [CuL] complexes are good catalysts for the enantioselective cyclopropanation of alkenes with alkyl diazoacetate, affording the cyclopropyl esters in up to 77% *ee*. Both the steric and electronic properties of R^1 but only the electronic properties of R^2 have a large effect on the reactivity and enantioselectivity of the [CuL]-catalyzed cyclopropanation reactions. The highest enantioselectivity results from the catalyst bearing the new Schiff-base ligand L^{11} (R^1 = Cl, R^2 = H) prepared in this work.

Experimental Section

General: The chiral Schiff-base ligands $H_2L^{1,2}$ and H_2L^{4-9} were prepared as reported previously.[33,36] The substituted salicylaldehydes used in the syntheses were prepared by literature procedures.[41] Solvents for catalytic cyclopropanation were purified according to standard procedures.[42] *cis*-β-Methylstyrene was prepared by hydrogenation of 1-phenyl-1-propyne (Aldrich) using Lindlar catalysts.[43] All other alkene substrates used for catalytic cyclopropanation were purchased from Aldrich or Fluka and were purified either by vacuum distillation or by passing through activated alumina. IR spectra were recorded on a Shimadzu IR-470 or Nicolet 20sxc FTIR spectrometer, and NMR spectra were recorded on a Jeol GSX-270, Bruker 300 DPX or Bruker 500 DRX spectrometer in $CDCl_3$ unless otherwise stated, with TMS as internal standard at ambient temperature. Mass spectra were measured on a Finnigan MAT 95 high-resolution mass spectrometer and UV/Vis/NIR spectra on a Lambda 19 spectrometer. Analytical HPLC was performed on a Beckmann model 331 HPLC system with a model 163 variable UV/Vis detector or Hewlett Packard Model 1050 HPLC system. Chiral HPLC measurements were performed on a commercial column (Daicel Chemical Industries, Ltd., Chirlcel OJ). Analytical GC was performed on a Hewlett−Packard 5890 series II system equipped with an HP 5890A flame ionization detector and an HP 3395 integrator.

Preparation of the 1,1′-Binaphthyl Schiff-Base Ligands H_2L^3 and H_2L^{10-13}: A mixture of (*S*)-2,2′-diamino-l,l′-binaphthyl (0.5 mmol for H_2L^3, 1.0 mmol for the others) and the corresponding salicylaldehyde derivative (2.1 equiv.) in ethanol (10 mL for H_2L^3, 30 mL for the others) was stirred at room temperature for 3 h, resulting in precipitation of an orange solid. The precipitate was collected by filtration and washed with ethanol. Recrystallization from dichloromethane/ethanol afforded the desired product as an orange crystalline solid.

(*S*)-2,2′-Bis(2-hydroxy-3,5-diiodobenzylideneamino)-1,1′-binaphthyl [(*S*)-H_2L^3]: Yield: 79%, m.p. 196−198 °C, [α] = +302.1 (*c* = 0.968, $CHCl_3$). IR (Nujol): ṽ = 3290−3650 (OH), 1611 cm^{-1} (C=N). ^1H NMR (270 MHz, $CDCl_3$): δ = 7.08 (d, $J_{4'',6''}$ = 2.44 Hz, 1 H, 4"-H), 7.18 (d, *J* = 8.31 Hz, 1 H, 5-H or 8-H), 7.26 (d, $J_{4'',6''}$ = 2.44 Hz, 1 H, 6"-H), 7.28−7.31 (m, 1 H, 6-H or 7-H), 7.44−7.50 (m, 1 H, 6-H or 7-H), 7.59 (d, $J_{3,4}$ = 8.79 Hz, 1 H, 4-H), 7.97 (d, *J* = 8.06 Hz, 1 H, 5-H or 8-H), 8.11 (d, $J_{3,4}$ = 8.78 Hz, 1 H, 3-H), 8.55 (s, 1 H, ArC*H*=NAr), 12.76 (s, 1 H, 2"-OH). ^{13}C NMR (270 MHz, $CDCl_3$): δ = 116.8, 120.4, 122.4, 123.1, 126.4, 126.5, 127.3, 128.5, 129.7, 130.5, 132.5, 132.9, 133.1, 142.8, 155.4, 160.4.

(*S*)-2,2′-Bis(5-chloro-2-hydroxybenzylideneamino)-1,1′-binaphthyl [(*S*)-H_2L^{10}]: Yield: 84%, m.p. 144−146 °C, [α] = +425.6 (*c* = 0.972, $CHCl_3$). IR (Nujol): ṽ = 3290−3650 (OH), 1611 cm^{-1} (C=N). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.62 (d, $J_{3'',4''}$ = 8.8 Hz, 1 H, 3"-H), 7.08 (d, *J* = 2.6 Hz, 1 H, 5-H or 8-H), 7.11 (d, *J* = 2.6 Hz, 1 H, 5-H or 8-H), 7.20−7.31 (m, 3 H, 6"-H, 6-H and 7-H), 7.44−7.49 (m, 1 H,), 7.63 (d, $J_{3,4}$ = 8.89 Hz, 1 H, 4-H), 7.97 (d, $J_{3'',4''}$ = 8.2 Hz, 1 H, 4"-H), 8.11 (d, $J_{3,4}$ = 8.8 Hz, 1 H, 3-H), 8.58 (s, 1 H, Ar′C*H*=NAr), 12.06 (s, 1 H, OH). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 116.4, 120.0, 123.3, 124.6, 126.2, 126.4, 127.2, 128.3, 129.9, 130.2, 131.0, 132.6, 132.7, 133.1, 143.0, 159.3, 160.3.

(*S*)-2,2′-Bis(3-chloro-2-hydroxybenzylideneamino)-1,1′-binaphthyl [(*S*)-H_2L^{11}]: Yield: 82%, m.p. 213−215 °C, [α] = +175.0 (*c* = 0.508, $CHCl_3$). IR (Nujol): ṽ = 3290−3650 (OH), 1611 cm^{-1} (C=N). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.25−7.31 (m, 1 H, 6-H or 7-H), 7.46−7.51 (m, 1 H, 6-H or 7-H), 7.58 (d, $J_{3,4}$ = 8.84 Hz, 1 H, 4-

H), 7.75−7.82 (m, 3 H, 4"-H, 5"-H and 6"-H), 8.00 (d, J = 8.17 Hz, 1 H, 5-H or 8-H), 8.08 (d, $J_{3,4}$ = 8.86 Hz, 1 H, 3-H), 8.59 (s, 1 H, Ar′CH=NAr), 12.79 (s, 1 H, OH). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 117.3, 121.3, 122.4, 123.9, 126.1, 126.5, 126.8, 127.1, 128.4, 129.5, 130.3, 130.6, 132.9, 133.7, 142.7, 156.6, 161.9.

(*S*)-2,2′-Bis(3-ethoxy-2-hydroxybenzylideneamino)-1,1′-binaphthyl [(*S*)-H_2L^{12}]: Yield: 75%, m.p. 228−230 °C, [α] = +382.7 (c = 0.980, $CHCl_3$). IR (Nujol): $\tilde{\nu}$ = 3075−3800 (OH), 1615 cm^{-1} (C=N). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (t, J = 7.0 Hz, 3 H, CH_3CH$_2$O-), 3.62 (q, J = 7.0 Hz, 2 H, CH$_3$CH_2O-), 6.65−6.81 (m, 2 H, 4"-H and 5"-H), 6.83 (d, J = 7.96 Hz, 1 H, 5-H or 8-H), 7.15−7.26 (m, 2 H, 6-H and 7-H), 7.38−7.44 (m, 1 H, 6"-H), 7.50 (d, $J_{3'',4''}$ = 8.77 Hz, 1 H, 4-H), 7.91 (d, J = 8.16 Hz, 1 H, 5-H or 8-H), 8.00−(d, $J_{3,4}$ = 8.77 Hz, 1 H, 3-H), 8.53 (s, 1 H, ArCH=NAr), 12.30 (s, 1 H, OH). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 14.75 (CH_3CH$_2$O), 64.6 (CH$_3$CH_2O), 116.4, 118.0, 118.1, 119.4, 124.1, 125.7, 126.5, 126.8, 128.3, 130.1, 132.4, 133.2, 144.7, 147.2, 151.2, 163.3.

(*S*)-2,2′-Bis(5-phenyl-2-hydroxybenzylideneamino)-1,1′-binaphthyl [(*S*)-H_2L^{13}]: Yield: 74%, m.p. 144−146 °C, [α] = +233.5 (c = 0.984, $CHCl_3$). IR (Nujol): $\tilde{\nu}$ = 3075−3800 (OH), 1619 cm^{-1} (C=N). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25−7.36 (m, 5 H, 3′-H, 4"-H, 6-H, 7-H and 5-H or 8-H), 7.39−7.47 (m, 5 H, Ar"′H), 7.49 (d, $J_{4'',6''}$ = 3.1 Hz, 1 H, 6"-H), 7.67 (d, $J_{3,4}$ = 8.87 Hz, 1 H, 4-H), 7.15−7.26 (m, 2 H, 6-H and 7-H), 7.38−7.44 (m, 1 H, 6"-H), 7.50 (d, $J_{3'',4''}$ = 8.77 Hz, 1 H, 4-H), 7.98 (d, J = 8.17 Hz, 1 H, 5-H or 8-H), 8.13 (d, $J_{3,4}$ = 8.83 Hz, 1 H, 3-H), 8.74 (s, 1 H, Ar′CH=NAr), 12.16 (s, 1 H, OH). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 116.8, 117.5, 119.4, 126.0, 126.5, 126.8, 127.1, 128.3, 129.6, 130.1, 130.4, 131.6, 132.0, 132.6, 133.2, 140.1, 143.7, 160.3, 161.8.

General Procedure for the Synthesis of [CuL]: A solution of $Cu(OAc)_2$ (1.5 equiv.) in methanol was added to a solution of binaphthyl ligand H_2L in dichloromethane. The mixture was stirred at room temperature for 3 h, resulting in precipitation of crude [CuL] as a dark green solid. The crude product was collected by filtration, washed with methanol and recrystallized with dichloromethane/ethanol or dichloromethane/pentane. Yield: close to 100%.

[CuL^1]: $C_{34}H_{18}Cl_4CuN_2O_2$ (691.9): calcd. C 59.02, H 2.62, N 4.05; found C 59.02, H 2.60, N 4.10. IR (KBr): $\tilde{\nu}$ = 1607 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 414 (19500), 652 nm (336). FAB MS: m/z = 690 [M + H]$^+$.

[CuL^2]: $C_{34}H_{18}Br_4CuN_2O_2$ (869.7): calcd. C 46.96, H 2.09, N 3.22; found C 48.10, H 2.22, N 3.01. IR (KBr): $\tilde{\nu}$ = 1600 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 414 (20900), 649 nm (384). FAB MS: m/z = 866 [M + H]$^+$.

[CuL^3]: $C_{34}H_{18}CuI_4N_2O_2$ (1057.7): calcd. C 38.61, H 1.72, N 2.65; found C 40.20, H 2.10, N 2.41. IR (KBr): $\tilde{\nu}$ = 1584 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 418 (21300), 640 nm (465). FAB MS: m/z = 1058 [M + H]$^+$.

[CuL^4]: $C_{50}H_{54}CuN_2O_2$ (778.5): calcd. C 77.14, H 6.99, N 3.60; found C 76.69, H 6.90, N 3.50. IR (KBr): $\tilde{\nu}$ = 1586 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 419 nm (25900), 647 nm (626). FAB MS: m/z = 778 [M + H]$^+$.

[CuL^5]: $C_{42}H_{36}Cl_2CuN_2O_2$ (735.2): calcd. C 68.61, H 4.94, N 3.81; found C 69.42, H 4.85, N 3.47. IR (KBr): $\tilde{\nu}$ = 1611 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 418 (24000), 648 nm (546). FAB MS: m/z = 734 [M]$^+$.

[CuL^6]: $C_{42}H_{36}Cl_2CuN_2O_2$ (735.2): calcd. C 68.61, H 4.94, N 3.81; found C 69.91, H 5.09, N 3.50. IR (KBr): $\tilde{\nu}$ = 1595 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 414 (19500), 652 nm (336). FAB MS: m/z = 734 [M + H]$^+$.

[CuL^7]: $C_{42}H_{36}CuN_4O_6$ (756.3): calcd. C 66.70, H 4.80, N 7.41; found C 65.96, H 4.50, N 7.38. IR (KBr): $\tilde{\nu}$ = 1595 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 371 (46000), 654 nm (398). FAB MS: m/z = 756 [M + H]$^+$.

[CuL^8]: $C_{38}H_{28}CuN_4O_6$ (700.2): calcd. C 65.18, H 4.03, N 8.00; found C 63.6, H 3.83, N 7.62. IR (KBr): $\tilde{\nu}$ = 1608 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 368 (56000), 651 nm (500). FAB MS: m/z = 700 [M + H]$^+$.

[CuL^9]: $C_{34}H_{20}CuN_4O_6$ (644.1): calcd. C 63.40, H 3.13, N 8.70; found C 65.20, H 3.13, N 8.50. IR (KBr): $\tilde{\nu}$ = 1607 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 357 (56700), 652 nm (419). FAB MS: m/z = 644 [M + H]$^+$.

[CuL^{10}]: $C_{34}H_{20}Cl_2CuN_2O_2$ (623.0): calcd. C 65.55, H 3.24, N 4.50; found C 63.50, H 3.87, N 4.11. IR (KBr): $\tilde{\nu}$ = 1608 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 412 nm (2120). FAB MS: m/z = 622 [M + H]$^+$.

[CuL^{11}]: $C_{34}H_{20}Cl_2CuN_2O_2$ (623.0): calcd. C 65.55, H 3.24, N 4.50; found C 64.44, H 3.61, N 4.15. IR (KBr): $\tilde{\nu}$ = 1604 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 404 (19500), 653 nm (321). FAB MS: m/z = 622 [M + H]$^+$.

[CuL^{12}]: $C_{38}H_{30}CuN_2O_4$ (642.2): calcd. C 71.07, H 4.71, N 4.36; found C 71.46, H 4.55, N 4.04. IR (KBr): $\tilde{\nu}$ = 1605 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 410 (26800), 653 nm (428). FAB MS: m/z = 642 [M + H]$^+$.

[CuL^{13}]: $C_{46}H_{30}CuN_2O_2$ (706.3): calcd. C 78.22, H 4.25, N 3.96; found C 77.58, H 4.28, N 4.10. IR (KBr): $\tilde{\nu}$ = 1619 cm^{-1} (C=N). Visible spectrum (CH_2Cl_2): λ_{max} (ε) = 422 (23500), 640 nm (625). FAB MS: m/z = 706 [M + H]$^+$.

X-ray Crystallography: Suitable crystals of ligand H_2L^{12} and complex [CuL^2] were obtained by recrystallization of the compounds from dichloromethane/ethanol. Diffraction data were collected on a Rigaku AFC7R diffractometer at ambient temperature. Intensity data were corrected for Lorentz and polarization effects. Absorption corrections based on the χ scan technique were also applied. The structure was solved by direct methods (SIR 92) and refined on F by least-squares analysis. The absolute structure of the molecule was determined by analysis of both configurations including the anomalous scattering effect. Hydrogen atoms were placed in their ideal positions (C−H: 0.95 Å) and included in the structure factor calculations but were not refined. All calculations were performed on a silicon Graphic workstation with the teXsan package.[44]

CCDC-171639 and -171640 contain the supplementary crystallographic data for this paper (excluding structure factors). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure for [CuL]-Catalyzed Diazoester Cyclopropanation of Styrene: A mixture of styrene (10 mmol) and [CuL] (0.5 mmol) was heated with stirring under nitrogen at 40 °C. To this mixture was added dropwise a solution of styrene (10 mmol) and ethyl or *tert*-butyl diazoacetate (5 mmol) over a period of 4 h. During this period, gas bubbles were evolved. The reaction was complete when no more bubbles were given off. The reaction products were isolated by column chromatography. The enantiomeric excess was measured by HPLC (Daicel Chemical Industries, Ltd., Chiral OJ column).

Relative Reactivity of Styrenes in the [CuL]-Catalyzed Cyclopropanation: In a typical competition reaction, equimolar amounts of styrene and substituted styrene (10 mmol each) and the copper

complex (0.5 mmol) were mixed in dichloromethane (5 mL) at 40 °C. To this mixture was added dropwise a solution of ethyl diazoacetate (1 mmol) over a period of 4 h. During this period, gas bubbles were evolved. The reaction was complete when no more bubbles were given off. The amounts of cyclopropyl esters formed were analyzed by GC and NMR spectroscopy.

Acknowledgments

We thank the Hong Kong Research Grants Council [PolyU 01/97C], Generic Drug Program of the University of Hong Kong, and City University of Hong Kong [CityU DAG 7100203] for financial support.

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Received October 5, 2001
[I01393]