European Journal of Chemistry 1 (4) (2010) 360-367

European Journal of Chemistry

Journal homepage: www.eurjchem.com

Chiral Cu(II) salen complexes catalyzed aerobic oxidative biaryl coupling-probing the reaction by EPR

Subbaramanian Sabarinathan, Gnanasambandam Vasuki* and Pillutla Sambasiva Rao

Department of Chemistry, Pondicherry University, Pudhucherry, IN-605 014, India

**Corresponding author at: Department of Chemistry, Pondicherry University, Pudhucherry, IN-605 014, India. Tel.: +91.413.2654498; fax: +91.413.2655987.*
E-mail address: vasukig@gmail.com (G. Vasuki).

ARTICLE INFORMATION

Received: 27 July 2010
Received in revised form: 29 September 2010
Accepted: 30 September 2010
Online: 31 December 2010

KEYWORDS

Biaryl coupling
Chiral copper salen complexes
Cross coupling
BINOL
Aerobic oxidation
EPR

ABSTRACT

Aerobic oxidative coupling of 2-naphthol to 1,1'-binaphthyl-2,2'-diol has been achieved using chiral/achiral copper salen complexes as catalyst. Moderate enantioselectivity was obtained for the reaction of 2-napthol with a coordinating substituent with a chiral salen complex. Unsubstituted 2-naphthol resulted in racemic 1,1'-binaphthyl-2,2'-diol only with all chiral complexes. Electron paramagnetic resonance spectroscopy has been used to understand the factors influencing the asymmetric induction.

1. Introduction

Transition metal complexes with chiral ligands play a significant role in catalyzed enantioselective reactions. Among all of the ligands, Jacobson chiral salen ligand is known as the previledged ligand as it is capable of complexing with several metal ions and stabilizes them in different oxidation states [1-5]. Moreover, the steric and electronic nature of the complex can be easily tuned. They are found to be efficient catalysts in several mechanistically different asymmetric reactions. The efficiency of these asymmetric catalysts in general is controlled by several molecular characteristics, such as symmetry, steric properties, electronic nature of the metal ion and the ligands, as well as the interaction of the substrate with the catalyst. A rational design of a chiral catalyst with improved performance can be achieved only by an understanding of the electronic and structural properties that influence the reaction.

The use of Electron paramagnetic resonance spectroscopy (EPR) as a tool to understand the mechanism of metal catalyzed asymmetric reactions is an emerging area of research [6-9]. Copper(II), an EPR active metal ion, has been used in several asymmetric oxidation reactions [10-18]. Use of oxygen present in air as oxidizing agent is gaining attention by being abundant and cost effective [19]. Enantioselective oxidative coupling of 2-naphthol is an important oxidation reaction in asymmetric synthesis [20-22]. Enantioselective oxidative coupling of 2-naphthol using chiral copper amine complexes has been attempted by several research groups [23-25]. Moreover copper N,N,N',N'-Tetramethylethylenediamine (TMEDA) complex is an effective catalyst for 1,1'-binaphthyl-2,2'-diol (BINOL) synthesis [26]. To the best of our knowledge, oxidative coupling of 2-naphthol to BINOL using chiral copper salen complexes using oxygen present in air is not reported. In this article, the results of aerobic oxidative coupling of 2-naphthol to BINOL catalysed by copper salen complexes have been reported. EPR has been used as a tool to explore the catalyst structure and mechanism of the reaction.

2. Experimental

2.1. Materials

Salicylaldehyde, 2-naphthol, and 2,4-di-ter-butyl phenol were purchased from Himedia and used without further purification. 1,2-Diaminocyclohexane purchased from Merck was resolved according to the literature procedure [27]. Formylation of 2,4-di-ter-butyl phenol and 2-naphthol was carried out by following the reported procedure [27,28].

2.2 Product identification

Melting points were determined in open capillary tubes on a MPA 120 melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer and chemical shift values are reported in δ units (parts per million) relative to Me_4Si as internal standard. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer in potassium bromide disc or neat thin film. Elemental analyses were carried out on Perkin-Elmer 2400 Series CHNS/O analyser. All the EPR spectra were recorded on a JEOL JES TE100 ESR spectrometer operating at X-band frequencies and having a 100 KHz modulation to obtain first derivative EPR spectrum. EPR spectra at 77 K were measured by immersing the sample in a quartz dewar filled with liquid nitrogen.

2.3 Preparation of ligands

All salen ligands were synthesized according to the reported procedure [29].

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
DOI:10.5155/eurjchem.1.4.360-367.221

2.4. Preparation of complexes

2.4.1. Preparation of complex 1

To a solution of (1*R*,2*R*)-[*N,N'-bis*(2'-hydoxybenzylidine)]-1,2-diaminocyclohexane (1.32 g, 4.1 mmol) in ethanol, $CuCl_2.2H_2O$ (0.69 g, 4.1 mmol) in ethanol was added. The reaction mixture was stirred for 3 h at ambient temperature then maintained at 5 °C. The compound formed was filtered and recrystallized from dichloromethane (30 mL) in less than 5 °C. Yield: 76%. Solubility: Sparingly soluble in $CHCl_3$, CH_2Cl_2, AcCN, acetone, EtOAc, MeOH, EtOH and soluble in DMSO. M.p.: 312 °C (dec). ESI mass M^+: 384. IR (KBr, cm^{-1}): 2932, 2858, 1630, 1603, 1545, 1393, 1345, 1305, 1282, 1199, 1152, 1026, 905, 801, 757. Anal. Calcd. for $C_{20}H_{20}CuN_2O_2$: C, 62.57; H, 5.25; N, 7.30. Found C, 62.95; H, 5.39; N, 7.40.

2.4.2. Preparation of complex 2

The complex was synthesized following the procedure described for complex **1** using (1*R*,2*R*)-[*N,N'-bis*(2'-hydoxy-3',5'-di-*t*-butyl-benzylidine)]-1,2-diaminocyclohexane, but methanol (30 mL) was used as solvent. Yield: 99%. Solubility: Sparingly soluble in MeOH, EtOH and soluble in $CHCl_3$, CH_2Cl_2, AcCN, acetone, EtOAc, DMF, DMSO, chlorobenzene, toluene. M.p.: 265-270 °C (dec). ESI mass M^+: 608. IR (KBr, cm^{-1}): 2954, 2866, 1621, 1526, 1462, 1432, 1346, 1322, 1254, 1165. Anal. Calcd. for $C_{36}H_{52}CuN_2O_2$: C, 71.07; H, 8.62; N, 4.60. Found C, 71.13; H, 8.57; N, 4.61.

2.4.3. Preparation of complex 3

The complex was synthesized following the procedure described for complex **1** using (1*R*,2*R*)-[*N,N'-bis*(2'-hydoxynaphthylidine)]-1,2-diaminocyclohexane. Yield: 99%. Solubility: soluble in $CHCl_3$, CH_2Cl_2, AcCN, acetone, EtOAc, DMF, DMSO. M.p.: not melted > 320 °C. ESI mass M^+: 484. IR (KBr, cm^{-1}): 2932, 2360, 1615, 1538, 1508, 1397, 1345, 1310, 1183, 1091, 1037, 827, 739. Anal. Calcd. for $C_{28}H_{24}CuN_2O_2$: C, 69.48; H, 5.00; N, 5.79. Found C, 69.55; H, 4.98; N, 5.74.

2.4.4. Preparation of complex 4

To a solution of *bis*(2'-hydoxybenzylidine)]-1,2-diamino benzene (1.89 g, 6 mmol) in ethanol $CuCl_2.2H_2O$ (1.02 g, 6 mmol) in ethanol was added. The reaction mixture was stirred for 6 h at ambient temperature then maintained at 5 °C. The compound formed was filtered and washed by dichloromethane (20 mL x 2). Yield: 57%. Solubility: soluble in $CHCl_3$, CH_2Cl_2, MeOH, EtOH, EtOAc, acetone, AcCN, DMF, DMSO. M.p.: 189 °C (dec). ESI mass M^+: 378. IR (KBr, cm^{-1}):1607, 1580, 1534, 1466, 1439, 1386, 1306, 1191, 1153, 1131, 1036, 977, 924,750. Anal. Calcd. for $C_{20}H_{14}CuN_2O_2$: C, 63.57; H, 3.73; N, 7.41. Found C, 63.66; H, 3.70; N, 7.49.

2.4.5. Preparation of complex 5

This was synthesized as described for complex **4** using *bis*(2'-hydoxy-3',5'-di-*t*-butyl-benzylidine)]-1,2-diamino benzene. Yield: 73%. Solubility: $CHCl_3$, CH_2Cl_2, EtOH, MeOH, chlorobenzene, toluene. M.p.: 272-280 °C (dec). ESI mass M^+: 602. IR (KBr, cm^{-1}): 2954, 1699, 1649, 1604, 1577, 1522, 1461, 1430, 1362, 1256, 1198, 744. Anal. Calcd. for $C_{36}H_{46}CuN_2O_2$: C, 71.79; H, 7.70; N, 4.65. Found C, 71.84; H, 7.77; N, 4.63.

2.4.6. Preparation of complex 6

This was synthesized as described for complex **4** using *bis*(2'-hydoxy-naphthylidine)]-1,2-diaminobenzene. Yield: 68 %. Solubility: sparingly soluble in CH_2Cl_2, $CHCl_3$, DMSO, DMF, and very less soluble in EtOAc, AcCN. M.p.: not melted > 320 °C. ESI mass M^+: 478. IR (KBr, cm^{-1}): 1607, 1574, 1533, 1457, 1398, 1364, 1282, 1190, 1095, 828, 737. Anal. Calcd. for $C_{28}H_{18}CuN_2O_2$: C, 70.36; H, 3.80; N, 5.86. Found C, 70.34; H, 3.77; N, 5.81.

2.5. Experimental procedure for oxidative coupling of 2-naphthol to BINOL

To a stirred solution of 2-naphthol (0.432 g, 3 mmol) in chlorobenzene (15 mL) was added chiral copper (II) Schiff-base complex **2** (0.036g, 0.06 mmol, 2 mol %) and the reaction mixture was refluxed for 48 h under aerobic atmosphere. Reaction mixture was stirred by magnetic stirrer at 600 rpm. After completion of the reaction, solvent was evaporated under reduced pressure. The residue thus obtained was purified by column chromatography on silicagel (100-200 mesh) using ethylacetate/hexane (1:4) as eluent. Evaporation of solvent yielded 1,1'-binaphthyl-2,2'-diol (0.322 g). Oxidative coupling with **(B)** and cross coupling reactions were performed under similar condition.

2.6. Experimental procedure for EPR monitoring of the aerobic oxidative coupling reaction

The reaction was conducted as mentioned above. A small portion of reaction mixture was collected from the reaction mixture and transferred to aqueous cell and EPR spectrum was recorded. After the measurement this solution was transferred to the reaction vessel. Thus the reaction was monitored for two days at regular intervals.

2.7. Identification of products

1,1'-binaphthyl-2,2'-diol **(C):** M.p.: 212-214 °C. ^1H NMR ($CDCl_3$, δ, ppm): 7.14-7.16 (m, 2H), 7.26-7.32 (m, 2H), 7.35-7.39 (m, 4H), 7.88-7.90 (m, 2H), 7.95-7.98 (m, 2H) 4.00-4.70 (broad s, 2H). ^{13}C NMR ($CDCl_3$, δ, ppm): 110.8, 117.7, 124.0, 124.2, 127.4, 128.3, 129.4, 131.3, 133.4, 152.7. IR (KBr, cm^{-1}): 3486, 3065, 2965, 2890, 1689, 1632,1540,1466,1262.

Dimethyl 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylate **(D):** M.p.: 270-272 °C. ^1H NMR ($CDCl_3$, δ, ppm): 4.05 (s, 6H), 7.14-7.16 (m, 2H), 7.32-7.36 (m, 4H), 7.90-7.93 (m, 2H), 8.68 (m, 2H), 10.70 (m 2H). ^{13}C NMR ($CDCl_3$, δ, ppm): 52.7, 114.1, 116.9, 123.9, 124.7, 127.2, 129.4, 129.7, 132.8, 137.2, 154.0, 170.5. IR (KBr, cm^{-1}): 3178, 2971, 2915, 2846, 1725, 1686, 1626, 1506, 1439, 1325, 1285, 1152, 799.

Methyl 2,2'-dihydroxy-1,1'-binaphthyl-3-carboxylate **(E):** M.p.: 178-180 °C. ^1H NMR ($CDCl_3$, δ, ppm): 4.08 (s, 3H), 7.06-7.08 (m, 1H), 7.16-7.20 (m, 1H), 7.22-7.24 (m, 1H), 7.30-7.40 (m, 4H), 7.86-7.95 (m, 4H), 8.74 (m, 1H), 10.85 (m, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 52.9, 114.0, 114.3, 114.5, 117.6, 123.4, 124.5, 124.6, 124.7, 126.6, 127.3, 128.3, 129.3, 129.8, 130.1, 130.2, 133.4, 133.9, 137.4, 151.4, 154.9, 170.3. IR (KBr, cm^{-1}): 3497, 2978, 2890, 1738, 1694, 1500, 1431, 1319, 1275, 1211, 1150, 999, 786.

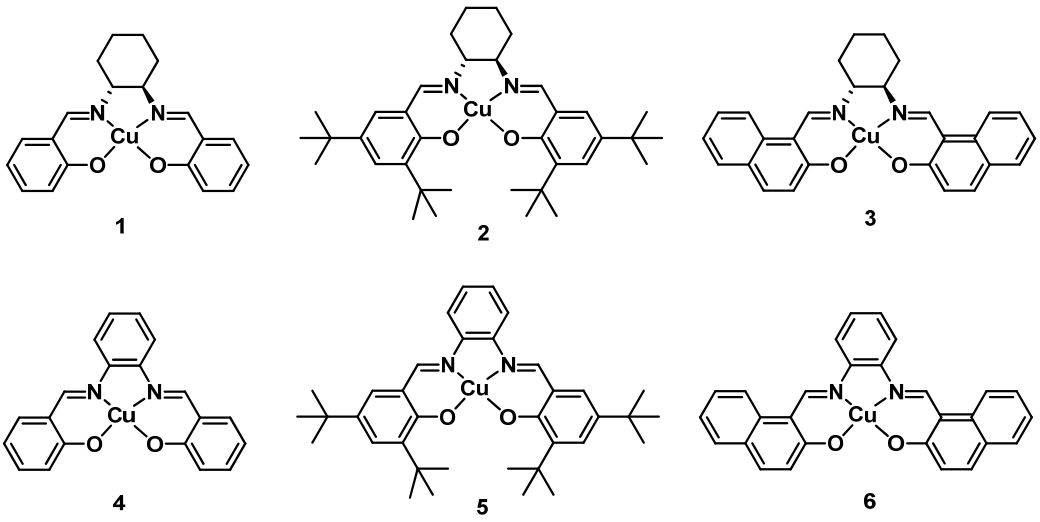


Figure 1. Copper salen complexes.

3. Results and discussion

3.1. EPR characterization of complexes

Three chiral salen ligands and three achiral salen ligands prepared using 1*R*,2*R*-cyclohexanediamine and 1,2-diamino benzene respectively were complexed with Cu(II) chloride (Figure 1). Complexes **1-6** were characterized by EPR. The EPR data are presented in Table 1.

EPR parameters indicate unique electronic and geometric arrangement around each complex (Figure 2). Complexes **1**, **3**, **4** and **6** show rhombic symmetry, while **2** and **5** show axial symmetry. While the powder EPR spectrum of **1** shows g_{II} and $g_{\perp}$ values, analogous complex **4** show isotropic value only. Complex **1** also shows super hyperfine splitting due to the interaction of two magnetically inequivalent nitrogens with copper whereas complex **4** does not shows such super hyperfine splitting. Both powder and solution EPR of complex **5** at room temperature and at LNT show two sets of g_{II} and $g_{\perp}$ values indicating the presence of two copper species. The powder EPR of **2** shows one g_{II} and $g_{\perp}$ values, but EPR of solution at LNT gives two sets of g_{II} and $g_{\perp}$ values similar to **5**. These complexes may adopt different conformations due to the presence of bulky tertiary butyl groups. Complex **3** and **6** show g_{iso} only at RT but solution sample at LNT shows three g values for both complexes confirming the rhombic symmetry.

In general chiral salen complexes **1-3** are more distorted than their achiral analogues **4-6**. The observed distortion can be attributed to the *trans* orientation of the amino groups in cyclohexanediamine.

3.2. Catalytic performance of complexes

All complexes were tested for their efficacy for aerobic oxidative coupling of 2-naphthol derivatives (Scheme 1-3). To optimize the reaction condition, oxidative coupling of 2-naphthol with complex **2** was performed in different polar as well as non-polar organic solvents like dichloromethane, dichloroethane, methanol, ethanol, acetone, tetrahydrofuron, carbontetrachloride, chloroform, ethylacetate, acetonitrile, xylene, tolune and chlorobenzene at room temperature and under reflux condition. Reaction in chlorobenzene under refluxing condition resulted in the optimum condition for the formation of the desired product BINOL. In other solvents either reaction did not yield BINOL or the yield of the product was very low. The reaction progress was monitored by TLC (SiO_2). Reaction time was optimised to be 48 h to obtain maximum yield of the desired product BINOL. Continuing the reaction beyond 48 h resulted in lowering the yield of BINOL, probably due to BINOL undergoing oxidation. Lowering the amount of catalyst resulted in lowering the conversion of 2-naphthol. The effect of the amount of catalyst used on the reaction is presented in Table 2.

Increasing the amount of catalyst decreased the yield of the desired product (**C**) with more byproducts. Therefore, the reaction was performed with 2 mol% of the catalyst **4-6**. Among all the complexes, **2** showed good conversion of the reactant (**A**) to (**C**). Catalyst **3** was less effective in converting (**A**) to (**C**). A blank experiment carried out without the catalyst under identical experimental conditions did not produce BINOL indicating the participation of the copper complex in the reaction path. The use of stoichiometric amount of complex **2** as oxidizing agent under nitrogen atmosphere did not yield the product indicating that oxygen is essential for the reaction. All reactions were continued for two days and the desired product was isolated by column chromatography. The efficacy of the catalyst **1-3** was also tested for reaction with (**B**) and in cross coupling reaction between **A** and **B** (Table 3 and 4).

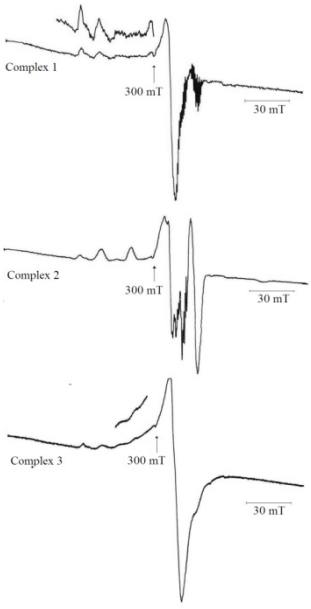
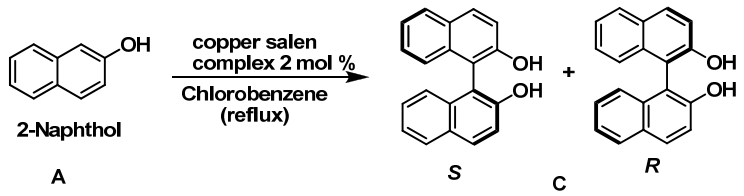


Figure 2. Solution EPR spectra of chiral complexes in LNT.

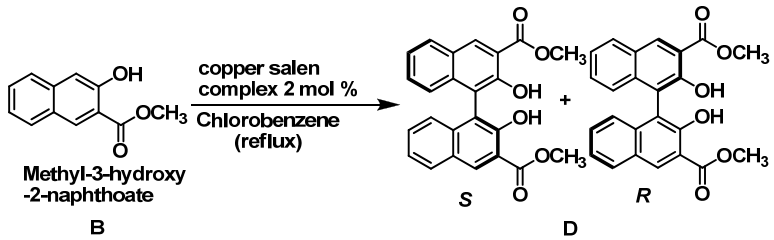
Table 1. EPR spectral data for the salen copper complexes.

Entry	Complex	Recorded condition		$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ mT	$A_{\perp}$ mT
1	1	RT	Powder	2.13	2.06	-	-
			Solution	2.10*	-	8.94*	-
		LNT	Powder	2.16	2.06	-	-
			Solution	g_1 =2.40	g_2 2.08	A_1=12.65	A_2=2.95
				g_3 =1.95		A_3=10.75	
2	2	RT	Powder	2.18	2.06	-	-
			Solution	2.09*	-	8.66*	-
		LNT	Powder	2.18	2.05	-	-
			Center 1[b]	2.26	2.09	24.43	4.14
			Center 2[b]	2.20	2.00	19.88	2.28
3	3	RT	Powder	2.07*	-	-	-
			Solution	2.10*	-	8.93*	-
		LNT	Powder	2.08*	-	-	-
			Solution	g_1 =2.40	g_2= 2.06	A_1=11.95	A_2=2.94
				g_3 =1.95		A_3=10.06	
4	4	RT	Powder	2.09*	-	-	-
			Solution	2.10*	-	10.46*	-
		LNT	Powder	2.41	2.09	11.91	-
			Solution	g_1 =2.41	g_2 2.08	A_1=12.33	A_2=3.34
				g_3 =1.95		A_2=10.66	
5	5	RT	Center 1[a]	2.29	2.09	17.89	2.77
			Center 2[a]	2.22	2.01	17.25	2.77
			Solution	2.08*	-	8.41*	-
		LNT	Center 1[a]	2.27	2.07	17.03	3.36
			Center 2[a]	2.22	2.01	16.61	3.58
			Center 1[b]	2.28	2.07	22.01	3.81
			Center 2[b]	2.21	1.99	19.68	1.27
6	6	RT	Powder	2.07	-	-	-
			Solution	2.10*	-	8.93*	-
		LNT	Powder	2.08*	-	-	-
			Solution	g_1 =2.40	g_2= 2.08	A_1=12.45	A_2=2.95
				g_3 =1.95		A_3=10.44	

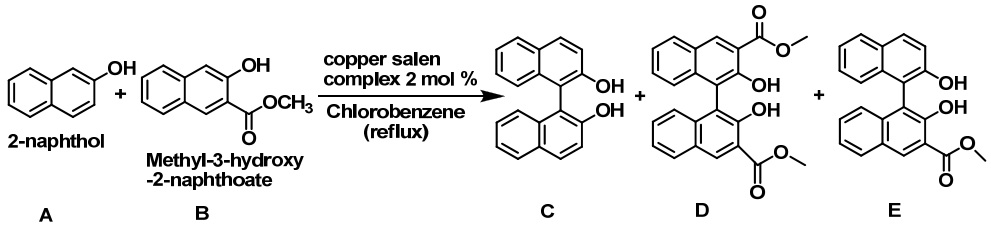
* Represents iso of the parameter.
[a] Corresponds to powder spectrum.
[b] Corresponds to LNT spectrum of solution.



Scheme 1



Scheme 2



Scheme 3

Table 2. Aerobic oxidation of 2-naphthol [a] with catalysts **1-6**.

Entry	Catalyst	Amount of catalyst (mol %)	Reaction Time (Hr)	Conversion[b] (%)	Yield[c] (%)
1	1	2	48	89	34
2	2	2	48	70	75
3	3	2	48	100	38
4	1	5	48	100	27
5	2	5	40	100	57
6	3	5	48	100	23
7	1	10	20	100	0
8	2	10	48	100	0
9	3	10	48	100	0
10	4	2	48	52	35
11	5	2	48	50	30
12	6	2	48	53	38

[a] 2-Naphthol (3 mmol), copper (II) salen complexes (2-10 mol %) in chlorobenzene (15 mL) at reflux temperature under aerobic atmosphere.
[b] Conversion refers to fraction of starting material consumed in the reaction.
[c] Yield refers to fraction of desired product with respect to conversion.

Table 3 Aerobic Oxidative coupling of methyl-2-hydroxy-3-naphthoate and 2-naphthol using 2 mol% chiral salen catalyst

Entry	Catalyst	Reaction Time(Hr)	Conversion[a] (%)	Selectivity[b] (C:D:E)	Yield[c] (%)
1	1	90	61	0: 0 : 100	40
2	2	50	51	0 : 5.23: 94.77	89
3	3	71	44	0 : 19.98: 80.02	80

[a] Conversion refers to fraction of starting material consumed in the reaction.
[b] Determined from isolated yields.
[c] Yield refers to fraction of cross coupled product with respect to conversion.

Table 4. Aerobic Oxidative coupling of methyl-2-hydroxy-3-naphthoate using 2 mol% chiral salen catalyst.

Entry	Catalyst	Reaction Time (Hr)	Conversion[a] (%)	Yield[b] (%)	*R:S*[c] (%)
1	1	48	80	55	31:69
2	2	48	25	100	50:50
3	3	48	58	42	50:50

[a] Conversion refers to fraction of starting material consumed in the reaction.
[b] Yield refers to fraction of desired product with respect to conversion.
[c] Determined by HPLC using DAICEL Chiralpak AD-H.

Catalyst **1** was more efficient in oxidative coupling of (**B**). Cross coupling reaction between (**A**) and (**B**) under similar conditions resulted in cross coupled product as the major product while substrate (**A**) disappeared completely from the reaction mixture forming (**E**) and byproducts, reactant (**B**) could be isolated from the reaction mixture. Homo coupled product (**C**) was not formed in this reaction and the yield of another homo coupled product (**D**) and the cross coupled product (**E**) are presented in Table 3. This observed selectivity in product formation may be ascribed to the electronic nature of the radical formed. Substrate (**B**) with an electron withdrawing group might act as an acceptor, and substrate (**A**) might participate in one electron red-ox reaction with copper (II) complex generating a radical intermediate which preferentially couples with substrate (**B**).

3.3. EPR monitoring of reaction

The reaction performed using catalyst **1** was monitored by EPR and TLC. There is no apparent difference in EPR spectra of the complex and of the reaction mixture till the formation of BINOL was noticed on TLC. However different EPR patterns are seen as the reaction was in progress and concentration of BINOL in the reaction mixture increased. Though the reaction is suggested to proceed through a radial mechanism, a free radical signal was not seen in the EPR spectrum till BINOL (**C**) was noted on TLC. Moreover, EPR pattern of the complex also did not show any change till the formation of BINOL was noted on TLC. The radical may be short lived and undergo dimerization before being detected by EPR. However, variations in the intensity of the copper lines were observed which is attributable to the red-ox cycle of the reaction. Formation of a new copper species and a radical signal was observed (Figure 3, 3g) as the reaction time increased. The free radical signal persisted till the completion of the reaction and increased in intensity (Figure 3, 3g-3k). The radical signal might arise from BINOL and the new copper species seen in the EPR might be due to the interaction of BINOL with the catalyst.

The observed decrease in the yield of (**C**) with concomitant increase in other by-products when the amount of the catalyst is increased can be attributed to an increase in the rate of the reaction with increasing the amount of the catalyst resulting in (**C**) and its reaction with the catalyst.

Monitoring the reaction of (**A**) using catalyst **2** also showed a similar trend in the EPR lines of copper as long as the reaction continued. Although EPR resonances corresponding to a radical appeared as observed in the reaction with catalyst **1**, the increasing intensity of the radical signal did not affect the pattern of the copper lines (Figure 4, 4i-4j) ascribable to the steric crowding around copper preventing the binding of BINOL to metal ion.

3.4. Stereoselectivity of biaryl coupling

Oxidative coupling of (**A**) with chiral catalysts **1-3** resulted in the formation of racemic BINOL only. However, oxidative coupling of (**B**) under similar conditions resulted in 38% ee (Figure 6) in the reaction with catalyst **1** (Table 4). But the reaction of (**B**) with catalysts **2** and **3** resulted in racemic products. A cross coupling reaction with catalysts **1-3** also resulted in racemic products only. These observations suggest that the presence of chelating substituents and less hindered catalysts enables the substrate to remain bound to chiral catalyst till the coupling reaction is completed (Scheme 4). Similar observation has been reported in chiral amine – copper complex catalyzed reactions [24].

EPR monitoring of the reaction does not show any change in the pattern of the EPR lines as long as the reaction occurred (Figure 5). Contrary to the reaction of (**A**) with catalyst **1**, a free radical signal and new copper specie did not appear as the reaction was in progress indicating that the product does not react with the catalyst.

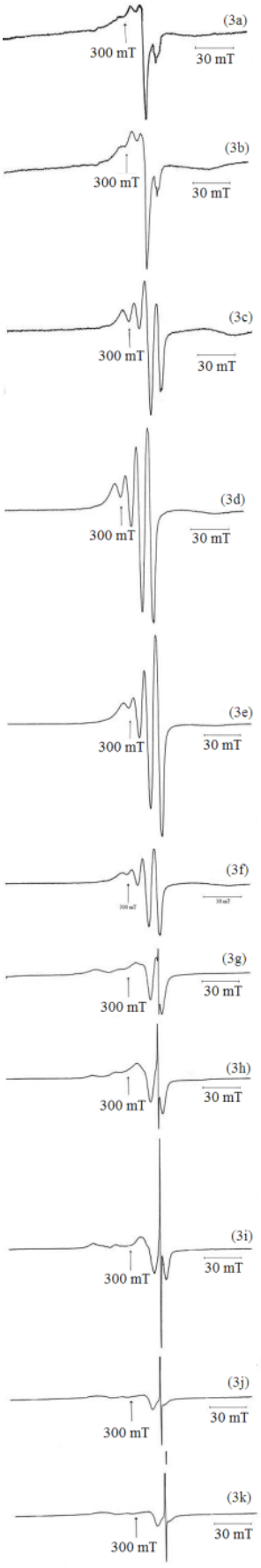


Figure 3. EPR monitoring of complex 1 with (**A**). (3a) complex in chlorobenzene; (3b) after addition of 2-naphthol; (3c) 30 min; (3d) 2.30 Hr; (3e) 3.30 Hr; (3e) 4.30 Hr; (3f) 5.30 Hr; (3g) 6.15 Hr; (3h) 6.45 Hr; (3i) 7.30 Hr; (3j) 10.00 Hr; (3k) 4 days.

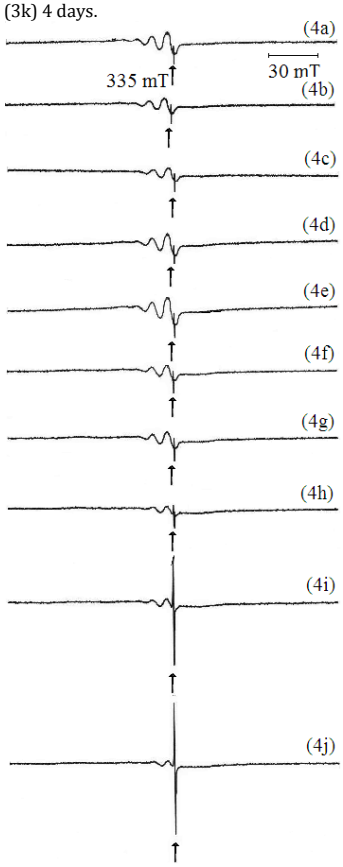


Figure 4. EPR monitoring of complex 2 with (**A**). (4a) complex in chlorobenzene; (4b) after addition of 2-naphthol; (4c) 2.30 Hr; (4d) 5.30 Hr; (4e) 25 Hr; (4f) 26.30 Hr; (4g) 28 Hr; (4h) 34 Hr; (4i) 35 Hr; (4j) 37.30 Hr.

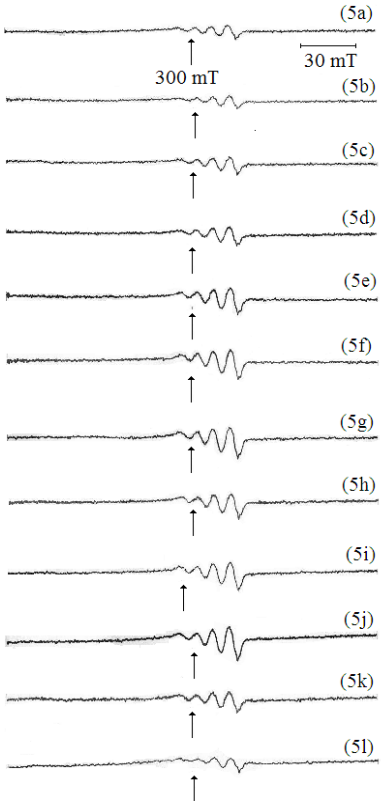


Figure 5. EPR monitoring of complex 1 with (**B**). (5a) complex in chlorobenzene; (5b) after addition of 2-naphthol; (5c) 1.00 Hr; (5d) 2.00 Hr; (5e) 4.00 Hr; (5f) 7.00 Hr; (5g) 9.00 Hr; (5h) 10.00 Hr; (5i) 15 Hr; (5j) 21.00 Hr; (5k) 30.00 Hr; (5l) 48.00 Hr.

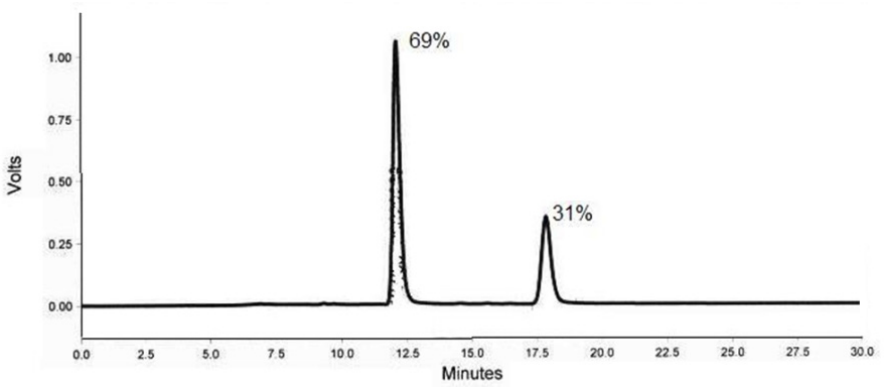
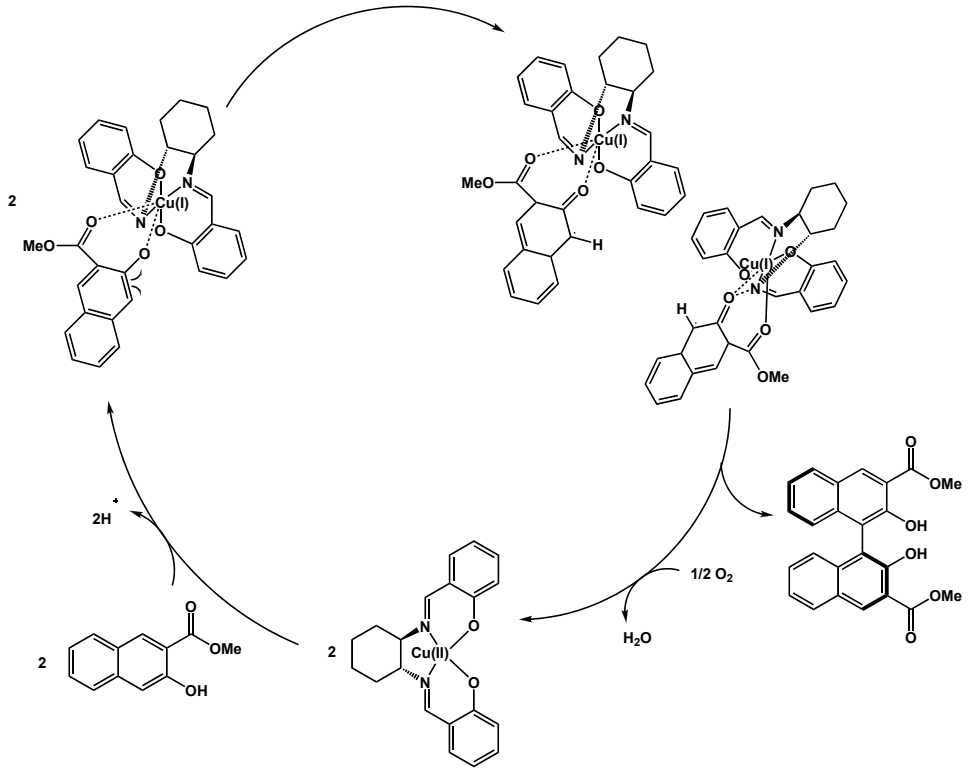


Figure 6. Chiral HPLC of dimethyl 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylate (**D**) from the coupling of (**B**) catalyzed by complex **1**.



Scheme 4

The observed enationselectivity supports that the reaction involves the participation of the catalyst, but binding of the substrate with the complex is not detectable by EPR. Lack of stereoselectivity of the reaction of (**B**) with catalysts **2** and **3** can be attributed to the steric crowding around the metal center preventing the chelation of the substrate with the complex.

4. Conclusion

Cu(II) salen complexes can be used as catalysts to bring out oxidative coupling of 2-naphthol derivatives. The catalytic efficiency depends on the extent of the distortion around Cu(II). The stereoselectivity of the reaction is influenced by the nature of substituent on the substrate as well as the steric crowding around the metal center. Biaryl coupling favors the formation of cross coupled product.

Acknowledgement

G.V. thanks the University Grants Commission (UGC) F. No. 32-238/2006(SR)) & Department of Science and Technology (DST), Government of India, New Delhi for financial support.

References

[1]. Venkataramanan, N. S.; Kuppuraj, G.; Rajagopal, S. *Coord. Chem. Rev.* **2005**, *249*, 1249-1268.
[2]. Baleizão, C; Garcia, H. *Chem. Rev.* **2006**, *106*, 3987-4043.
[3]. Achard, T. R. J.; Clutterbuck, L. A.; North, M. *Synlett* **2005**, *12*, 1828-1847.
[4]. Gupta, K. C.; Sutar A.K. *Coord. Chem. Rev.* **2008**, *252*, 1420-1450.
[5]. Cozzi, P.G. *Chem. Soc. Rev.* **2004**, *33*, 410-421.
[6]. Traa, Y; Murphy, D. M.; Farley, R. D.; Hutchings, G. J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1073-1080.
[7]. Bolm, C; Martin, M.; Gescheidt, G.; Palivan, C.; Neshchadin, D.; Bertagnolli, H.; Feth, M.; Schweiger, A.; Mitrikas, G.; Harmer J. *J Am. Chem. Soc.* **2003**, *125*, 6222-6227.

[8]. Bolm, C.; Martin, M.; Gescheidt, G.; Palivan, C.; Stanoeva, T.; Chem, D.; Bertagnolli, H.; Feth, M.; Schweiger, A.; Mitrikas, G.; Harmer J. *Chem. Eur J.* **2006**, *13*, 1842-1850.
[9]. Doorslaera, S. V.; Caretti, I.; Fallis, I. A.; Murphy, D. M. *Coord. Chem. Rev.* **2009**, *253*, 2116-2130.
[10]. Zhu, H. B.; Dai, Z. Y.; Huang, W.; Cui, K.; Gou, S. H.; Zhu, C. J. *Polyhedron* **2004**, *23*, 1131-1137.
[11]. Liu, B.; Zhu, S.F.; Wang, L. X.; Zhou, Q. L. *Tetrahedron: Asymmetry* **2006,** *17*, 634-641.
[12]. Minato, D.; Arimoto, H.; Nagasue, Y.; Demizu, Y.; Onomura O. *Tetrahedron* **2008**, *64*, 6675-6683.
[13]. Bolm, C.; Schlingloff, G.; Bienewald, F. *J. Mol. Catal.* **1997**, *117*, 347-350.
[14]. Hoang, V. D. M.; Reddy, P. A. N.; Kim, T. J. *Organometallics* **2008**, *27*, 1026- 1027.
[15]. Ginotra, S. K.; Singh, V. K. *Org. Biomol. Chem.* **2006**, *4*, 4370-4374.
[16]. Mimmi, M. C.; Gullotti, M.; Santagostini, L.; Battaini, G.; Monzani, E.; Pagliarin, R.; Zoppellarod, G.; Casella, L. *Dalton Trans* **2004**, 2192-2201.
[17]. Ginotra, S. K.; Singh, V. K. *Tetrahedron* **2006**, *62*, 3573-3581.
[18]. Alamsetti, S. K.; Mannam, S.; Mutupandi, P.; Sekar, G. *Chem. Eur. J.* **2008**, *15*, 1086-1090.
[19]. Punniyamurthy, T.; Velusamy, S.; Iqbal, J. *Chem. Rev.* **2005**, *105*, 2329-2363.
[20]. Pu, L. *Chem. Rev.* **1998**, *98*, 2405-2494.
[21]. Chen, Y.; Yekta, S.; Yudin, A. K. *Chem. Rev.* **2003**, *103*, 3155-3211.
[22]. Brunel, J. M. *Chem. Rev* **2005,** *105*, 857-897.
[23]. Smrčina, M.; Poláková, J.; Vyskočil, S.; Kočovský, P. *J. Org. Chem.* **1993**, *58*, 4534-4538.
[24]. Nakajima, M.; Miyoshi, I.; Kanayama, K.; Hashimoto, S. I.; Noji, M.; Koga, K. *J. Org. Chem.* **1999**, *64*, 2264-2271.
[25]. Li, X.; Hewgley, J. B.; Mulrooney, C. A.; Yang, J.; Kozlowski, M. C. *J. Org. Chem.* **2003**, *68*, 5500-5511.
[26]. Noji, M.; Nakajima, M.; Koga, K. *Tetrahedron letter* **1994**, *35*, 7983-7984.
[27]. Larrow, J. F.; Jacobsen, E. N. *J. Org. Chem.* **1994**, *59*, 1939-1942.
[28]. Kalechits, G. V.; Osinovskii, A. G.; Matveenko, Y. V.; Ol'khovik, V. K. *Russ. J. Appl. Chem.* **2002**, *75*, 962-964.
[29]. Kureshy, R. I.; Khan, N. H.; Abdi, S. H. R.; Patel, S. T.; Jasra, R. V. *Tetrahedron: Asymmetry* **2001**, *12*, 433-437.