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Original Scientific Paper

Structural Properties of Some C_2-Symmetric Schiff Bases and Stereoselectivity in Cyclopropanation of Styrene by Their Cu(I) Complexes*

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C_2-symmetric Schiff bases derived from *R*-camphor and *R*-fenchone (**1–6**) were prepared, their configurational and conformational features determined by 1D- and 2D-NMR spectra and supported by MM2 calculations. Their Cu(I) complexes prepared *in situ* were examined in cyclopropanation of styrene and low to medium e.e.'s (2–32%) were obtained. Correlation of the structure of *E,E*-**1** and *Z,Z*-**6** with enantioselectivity of their Cu(I) complexes revealed restricting steric requirements in the former, possessing *gem* dimethyl group in the proximity of the chiral centre, near to the coordination sphere of alkene and carbene, as the probable origin of its higher enantioselectivity.

INTRODUCTION

C_2 axis of symmetry in chiral bidentate ligands has generally been demonstrated to increase the enantioselectivity in various reactions catalyzed by their metal complexes. Recently, metal complexes of a series of bidentate nitrogen ligands with two planar five-membered rings were used with great success in homogenous catalysis. These ligands can be represented by the general formula **I**, where endocyclic C=N bonds in the heterocyclic ring are also *endo* to the chelate ring formed in the catalytic complex. To such C_2 symmetric bidentate ligands belong semicorrines (A = C–CN, X = CH_2),[1] bi-

* Dedicated to the memory of Prof. Stanko Borčić, deceased in 1994.
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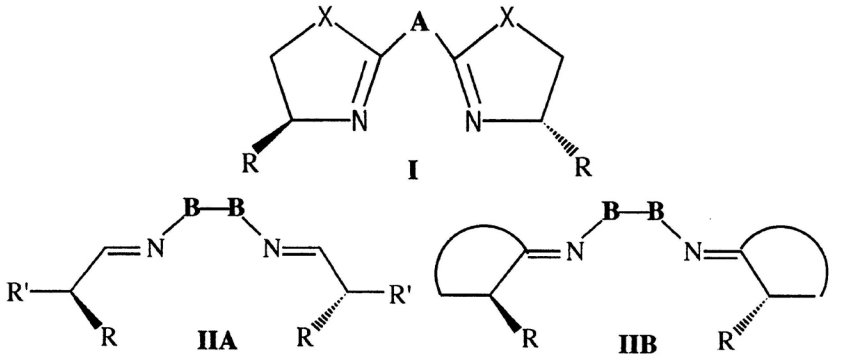
oxazolines (A = 0, X = O) and bis-oxazolines (A = CH_2 or CR_2, X = O),[2] and bi-thiazolines (A = 0, X = S).[3] C_2 symmetric bidentate Schiff bases represented by the general formula **IIA,B** differ from those represented by formula **I** in that two C=N bonds are *exo* to the chelate ring, and the chiral centre is in β-position to the coordinating N-atom.



In the bidentate ligands **I**, two stereogenic centres are regularly placed outside the chelate ring,[1–3] and **A** is regularly an achiral moiety or nil. In ligands **II**, however, the chiral centre can be found either in the ring,[4–8] or outside the chelate ring.[9] In the former case, **B–B** bears two stereogenic centres (as in CHR''–CHR'') and R = R'; in the latter case, **B–B** is an achiral moiety (*e.g.* CH_2–CH_2) and R ≠ R'. Representatives of the former group are chiral salen-derivatives[4] and *trans*–1*R*,2*R*–1,2-diaminocyclohexane benzylidene derivatives,[5–8] whereas representatives of the latter group are Schiff bases of the aldehyde derived from camphor.[9] Both types of ligands afforded complexes which are highly enantioselective catalysts for specific reactions, *e.g.* cyclopropanation,[1a,c,2a–d] aziridination[2e,6] and epoxidation[4,5] of olefins, conjugate reduction of α,β-unsaturated carboxylic esters[1d] and amides,[1e] hydrogen transfer reduction[2c,8] and hydrosilylation of ketones,[2j,3] palladium-catalyzed allylic alkylation,[1f,2c] Diels-Alder reaction[2f,g,7] and enantioselective conversion of aldehydes to cyanohydrins.[2h] All the C_2 symmetric ligands of type **IIA** with achiral subunit **B–B** prepared so far possess a chiral centre connected to the carbon of N=C group by a single **B–B** free rotating bond. This feature enables both achiral subunits to adopt many energetically similar conformations also in the catalytic complex, enhancing the number of possible, conformationally different catalytic species.

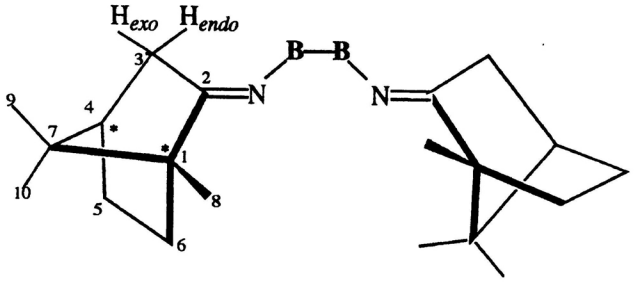
In continuation of our programme on the synthesis and evaluation of simple and inexpensive chiral nitrogen ligands in homogeneous catalytic reactions,[10–13] we decided to use chiral, conformationally rigid cyclic ketones, which are expected to form stereoselectively *Z*- or *E*- Schiff bases with simple diamines (**IIB**), and to study the effect of the conformationally fixed

proximal chiral centre and the size of the chelate ring, defined by the structure of the spacer, diamine subunit N–B–B–N, on the enantioselectivity in cyclopropanation.

RESULTS AND DISCUSSION

Synthesis of Ligands

Bidentate Schiff bases **1–6** were prepared by condensation of aliphatic or aromatic diamines with *R*-camphor and *R*-fenchone as sources of chirality. Their formation required prolonged reaction times and continuous elimination of water from the high boiling solvent. The best results were obtained

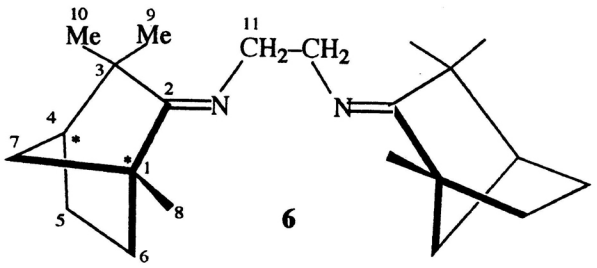


B—B **B—B**

1 **4**

2 **5**

3



6

by the procedure that uses *para*-toluensulphonic acid as catalyst in boiling toluene, and phosphorus pentoxide on the inert support for binding water out of the condensate.[12]

Configurational and Conformational Properties of the Ligands

Structural analysis of ligands was undertaken in order to correlate their structural properties with catalytic activity of their Cu(I) complexes. Combining the ^{1}H-, ^{13}C- and 2D-NMR data with computer modeling, using MM2 molecular mechanics, configurational and conformational analyses of the prepared ligands were performed.

^{13}C-NMR spectra of ligands **1–6** reveal no mixture of structural isomers around the C=N bond. In order to ascribe *E* or *Z* configuration to ligands **1–6**, ^{1}H-NMR and ^{13}C-NMR spectra of camphor and fenchone were first completely assigned, Tables I and II. To this aim, also 2D-NMR experiments, HETCOR, COSY and NOESY, were run. NOESY spectra of **1–3** show interaction between protons at C11 in the aliphatic bridge (H-11) and those in *endo* positions at C3 of the camphoric residue (H-3$_{endo}$). This interaction reveals that the aliphatic bridge is oriented *Z* to C3 atoms, and *E* to C1 atom, *i.e.* that ligands **1–3** possess *E,E* configuration.

Comparison of the ^{1}H-NMR spectra of **1** and **6** revealed that both contain multiplets centered at 3.47 and 3.73 ppm for CH_2CH_2 bridge, three singlets at 0.74, 0.91 and 0.93 ppm for Me-8, Me-9 and Me-10 in **1**, and at 1.24, 1.21 and 1.10 ppm for Me groups in **6**, respectively. In the NOESY spectra of **1**, the interaction between the multiplet centered at $\delta = 3.47$ ppm, risen by H-11 and resonances of H-3$_{endo}$ at $\delta = 1.95$–1.70 ppm, can be clearly observed, though superimposed by other protons (Figure 1, A), whereas the NOESY spectrum of **6** was more difficult to interpret. Only repeated slicing of the spectra revealed the interaction between the middle peak of three singlets, arising from the three Me groups at 1.21 ppm, and resonances of H-11 at $\delta = 3.73$ ppm. (Figure 1, B). Since the NOESY spectrum of **6** revealed additional interaction between two Me groups at 1.21 and 1.10 ppm, we concluded that they are geminally situated. Consequently, one of these geminal groups, and not the isolated Me-8 group, is in interaction with methylenic protons of the bridge, confirming *Z,Z* configuration around the C=N bond in **6**.

This picture of distribution of configurational species of **1**,**4** and **6** is supported by computer modeling using MM2 molecular mechanics for the three possible stereoisomers (*E,E*, *E,Z* and *Z,Z*). Calculations indicated an energy minimum for the *E,E*-configuration of ligands **1** and **4**, and for the *Z,Z*-configuration of ligand **6**, which is in agreement with the results obtained from the NMR data for ligands **1** and **6**. Ball & Stick models of *E,E*-**1** and *Z,Z*-**6** are presented in Figure 2.

TABLE I

^{1}H chemical shift data (δ/ppm) of camphor, fenchone and Schiff bases **1–6** in deuterochloroform at 25 °C

Proton	Camphor	**1**	**2**	**3**	**4**	**5**	Fenchone	**6**
H-3$_{exo}$	2.36	2.41	2.33	2.32	2.21	2.20		1.78–1.26
H-3$_{endo}$	1.85	1.95–1.70	1.92–1.76	1.94–1.77	1.89–1.62	1.89–1.71		1.78–1.26
H-4	2.09	1.95–1.70	1.92–1.76	1.94–1.77	1.89–1.62	1.89–1.71	2.13	1.78–1.26
H- 5$_{endo}$	1.93	1.95–1.70	1.92–1.76	1.93–1.79	1.89–1.62	1.89–1.71	1.81–1.66	1.78–1.26
H-6$_{endo}$	1.43–1.25	1.64	1.65	1.69–1.58	1.89–1.62	1.89–1.71	1.81–1.66	1.78–1.26
H-6$_{exo}$	1.68	1.33	1.34	1.34	1.50	1.51	1.61–1.51	1.78–1.26
H-5$_{exo}$	1.43–1.25	1.19	1.18	1.18	1.24	1.22	1.43–1.33	1.78–1.26
H-7							1.81–1.66	1.78–1.26
H-7							1.61–1.51	1.78–1.26
Me-8	0.91	0.74	0.74	0.74	0.87	0.85	1.14	1.24
Me-9	0.84	0.91	0.92	0.92	0.94	0.96	1.03	1.21
Me-10	0.96	0.93	0.96	0.96	1.02	1.08	1.03	1.10
H-11		3.47	3.25	3.23				3.73
H-12			1.92–1.76	1.69–1.58	6.96	6.13		
H-13					6.62	6.39		
H-14						7.16		

TABLE II

^{13}C chemical shift data (δ/ppm) of camphor, fenchone and Schiff bases **1–6** in deuterochloroform at 25 °C

Carbon	Camphor	**1**	**2**	**3**	**4**	**5**	Fenchone	**6**
C1	57.45	53.28	53.20	53.21	53.67	53.63	53.79	52.22
C2	219.32	182.33	181.71	181.47	184.76	184.95	223.23	184.17
C3	42.82	35.63	35.09	35.15	36.79	35.93	47.01	43.86
C4	43.06	43.68	43.57	43.62	45.57	43.53	44.97	49.62
C5	26.83	27.24?	27.21	27.25	27.09	27.15	24.57	25.07
C6	29.69	31.95?	31.92	31.96	32.00	31.80	31.46	33.61
C7	46.54	46.66	46.62	46.63	47.78	46.94	41.29	42.21
C8	9.02	19.41	19.28	19.30	19.75	19.80	14.23	24.71
C9(10)	19.54	18.68	18.68	18.71	18.79	18.76	22.97	23.95
C10(9)	18.91	11.15	11.16	11.18	10.95	10.93	21.31	17.59
C11		53.04	49.91	52.06	142.16	153.14		52.31
C12			31.16	28.33	123.31	110.17		
C13					119.81	113.99		
C14						129.29		

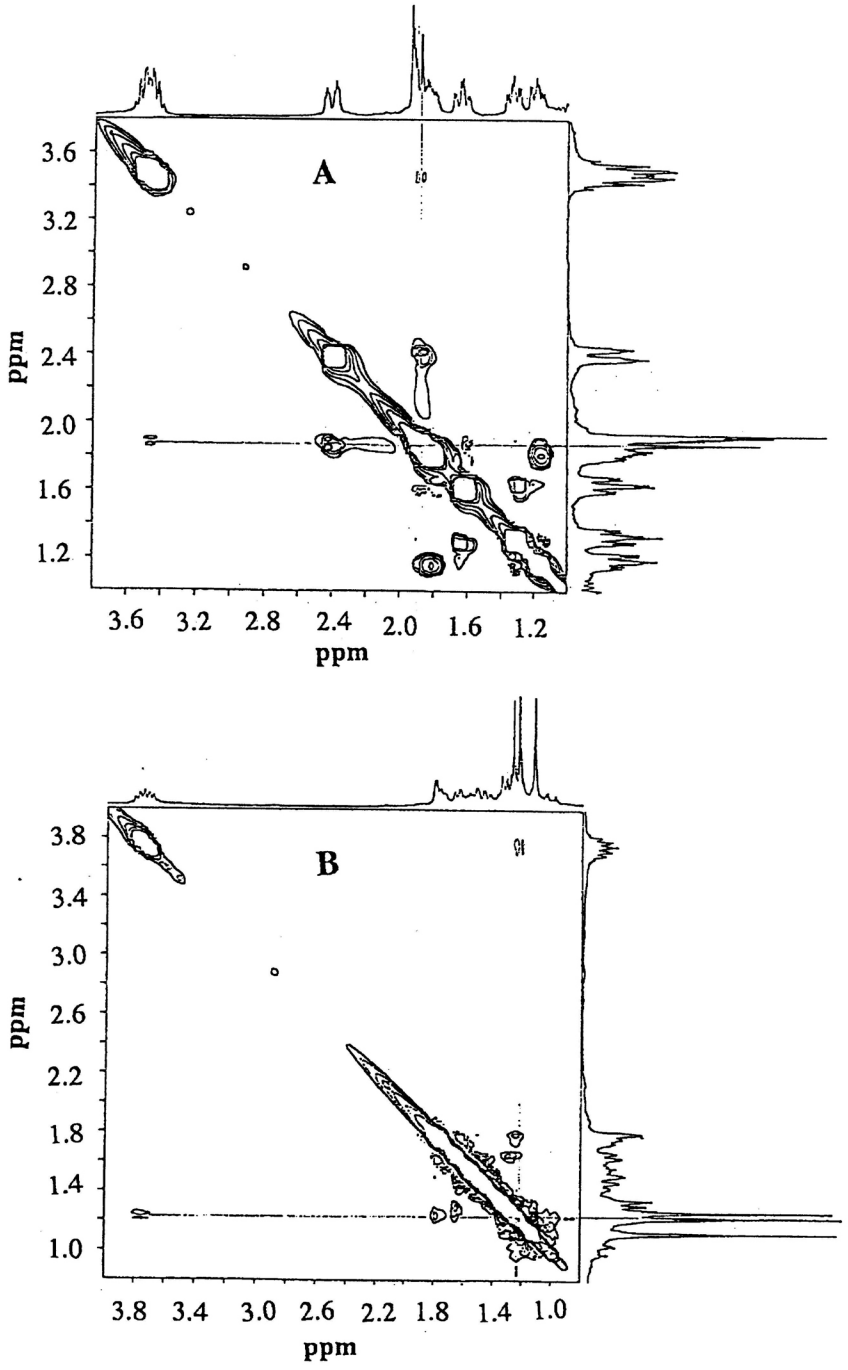
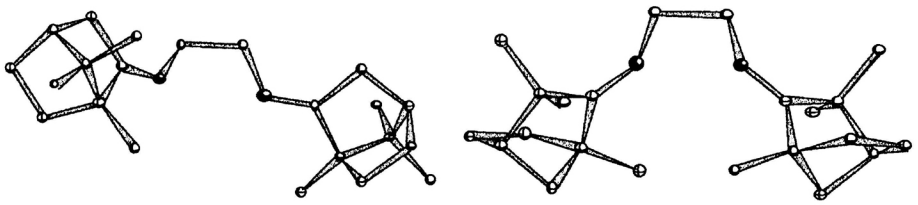


Figure 1. NOESY spectrum of ligand **1** (A) and ligand **6** (B).



E,E–**1** *Z,Z*–**6**

Figure 2. Ball & Stick models of the non hydrogen atoms of ligands *E,E*-**1** and *Z,Z*-**6** based on the MM2 calculations.

For the three stereoisomers of ligands **1** and **6** two rather shallow energy minima for the rotation around C11–C11' bond were found. They corresponded to the two conformers characterized by dihedral angles (N–C11–C11'–N') of *ca.* 70 and 180 degrees for **1**, and *ca.* 60 and 180 degrees for **6**. One can observe a clear difference in the minimal energies and heats of formation for the three calculated stereoisomers of **1**, but no significant differences for the three stereoisomers of **6**, revealing the *ZZ*-conformer characterized by dihedral angle (N–C11–C11'–N') at –58 degrees as the most stable, Table III.

Due to repulsion of the two nitrogen lone pairs, all three calculated stereoisomers of compound **4** display significant deviation of both camphoric subunits from coplanarity. Through rotation around N–C11 bond, they can

TABLE III

Minimal energy, heat of formation and dihedral angle α (N–C11–C11'–N') for *E,E*-, *E,Z*- and *Z,Z*-isomers of compounds **1** and **6**

Compound	Configuration	MMXE/ (kcal/mol)	HF/(kcal/mol)	α/deg
1	*E,E*	61.96	5.85	–70.50
		63.65	7.55	–179.92
	E,Z	64.66	8.55	–69.15
		65.81	9.70	–179.70
	Z,Z	68.74	12.63	–69.21
		68.67	12.56	–179.83
6	*E,E*	62.19	6.09	–60.40
		62.29	6.19	–179.87
	E,Z	62.10	5.99	–62.82
		62.05	5.94	–179.04
	Z,Z	60.17	4.07	–58.55
		62.10	5.99	–179.61

adopt *cisoid* or *transoid* arrangement. The calculated relative stabilities of the conformers, given in Table IV, show that the preferred conformer in all three stereoisomers is the *transoid* one, as an outcome of the minimized steric interactions between two bulky camphoric subunits. The differences between the energetically preferred *transoid* and disfavoured *cisoid* conformers were estimated at *ca.* 3–5 kcal/mol.

Ball & Stick models of *EE*-**4** in Figure 3. illustrate the stretched arrangement of the *cisoid* conformer and unstretched arrangement of the *transoid* conformer.

TABLE IV

Minimal energy, heat of formation and dihedral angles α_1 (C2–N–C11–C12), α_2 (C12'–C11'–N'–C2') and α_3 (N–C11–C11'–N') for *E,E*-, *E,Z*- and *Z,Z*-isomers of compound **4**

Configuration	Conformation	MMXE kcal/mol	HF kcal/mol	Dihedral angles/deg α_1	α_2	α_3
E,E	*transoid*	85.77	65,54	–111.53	–111.43	8.41
	cisoid	89.02	67.36	–61.16	67.66	2.10
	cisoid	88.01	66.67	–121.59	44.73	2.29
E,Z	*transoid*	87.22	67.74	–102.02	–118.89	3.01
	transoid	87.09	69.53	–99.66	–102.18	1.51
	cisoid	90.48	70.86	–86.67	52.39	5.62
Z,Z	*transoid*	89.54	71.66	–101.58	–101.56	–1.08
	cisoid	94.49	73.47	–74.19	59.66	3.40
	cisoid	94.04	74.73	–87.59	49.79	3.22

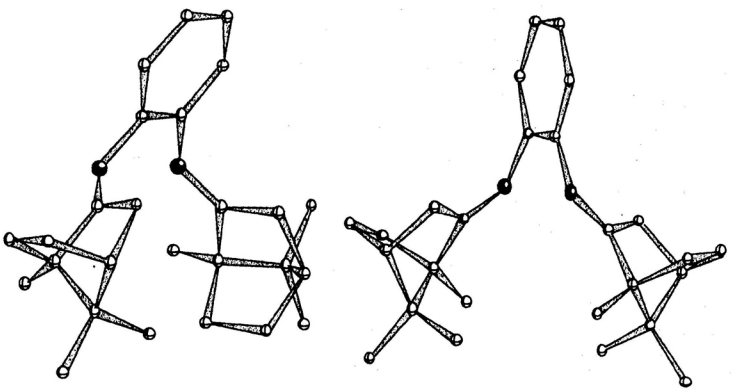


Figure 3. Ball & Stick models of the non hydrogen atoms of the *cisoid* and *transoid* conformers of *E,E*-**4** according to the force field calculations.

Catalytic Activity of Cu(I) Complexes of Ligands ***1-6***

Cu(I) complexes prepared *in situ* from Schiff bases **1–6** and Cu(I) trifluoroacetate have been examined in cyclopropanation of styrene with ethyldiazoacetate according to the reported protocol.[2d,13] Complex of the ligand **1** emerged as the most selective catalyst, affording 30% e.e. for the *cis* isomer of ethyl 2-phenyl-cyclopropane carboxylate and 32% e.e. for the *trans* isomer, Table V.

TABLE V

Enantioselectivity of cyclopropanation of styrene catalyzed by Cu(I) complexes of **1–6** at ligand/Cu ratio 1.3 : 1

Ligand	Yield / %	*cis*/*trans* / %	*cis* (e.e./%)	*trans* (e.e./%)
1	71	40/60	30 (1*R*,2*S*)	32 (1*R*,2*R*)
2	76	39/61	5 (1*R*,2*S*)	7 (1*S*,2*S*)
3	71	43/57	9 (1*R*,2*S*)	2 (1*R*,2*R*)
4	72	38/62	14 (1*R*,2*S*)	8 (1*R*,2*R*)
5	62	38/62	4 (1*R*,2*S*)	2 (1*R*,2*R*)
6	78	42/58	15 (1*R*,2*S*)	15 (1*R*,2*R*)
no	66	45/55	0	0

The enantioselectivity of cyclopropanation with the Cu(I) complex of **1** is double that obtained with **6**. At a first glance this is an unexpected result since both ligands possess a chiral centre bearing one Me group on the side of the chelate ring, in the proximity of the bound alkene and carbene, enabling chiral control of the enantioface-selective binding. On the basis of low e.e. with the complex of **6**, one would expect ligand **6** to possess *E,E* configuration. Indeed, this stereoisomer would have a chiral centre away from the chelate ring, and *gem* dimethyl unit close to the ring. Low enantioselectivity obtained with *Z,Z*-**6** could be explained by the larger distance of the *gem* dimethyl group from the coordination sphere of Cu ion, as compared to that in the camphor derivative *E,E*-**1**.

Ligand **4**, containing rigid *ortho*-phenylene moiety bridging two chiral subunits with two conjugated azomethine bonds, seems to be suitable for forming a stable 5-membered planar chelate ring with copper. It possesses an extended, 6π conjugated or 10π cross-conjugated, electronic structure, and consequently represents a softer donor and better π-acceptor than ligands **1–3** or **6**[14]. Force field calculations revealed, however, that the more flexible ethylene bridge in **1** allows copper atom in the catalytic complex to accommodate camphoric units close to the »fence« conformation, whereas the rigid phenylene bridge in **4** precludes such conformation, pushing electron

pairs of two nitrogen atoms out of coplanarity. This consideration could explain the eventually higher enantioselectivities (30% e.e. for *cis*- and 32% e.e. for *trans*-isomer) achieved with the Cu(I) complex of ligand **1**, than with ligand **4** (14% e.e. for *cis*- and 8% e.e. for *trans*-isomer).

Systematic variation of the ligand **1**/Cu ratio and temperature revealed no improvement of stereoselectivity, Table VI, decrease of temperature resulted in even somewhat lower enantioselectivity.

TABLE VI

Enantioselectivity of cyclopropanation of styrene catalyzed by Cu(I) complexes of **1** at different temperatures and different ligand/Cu ratios

Ligand/Cu ratio	Temp. °C	Yield %	*cis/trans* %	*cis* (e.e./%)	*trans*(e.e./%)
1.3	0	42	36/64	12 (1*R*,2*S*)	12 (1*R*,2*R*)
1.3	18	71	40/60	30 (1*R*,2*S*)	32 (1*R*,2*R*)
1.3	25	71	40/60	29 (1*R*,2*S*)	31 (1*R*,2*R*)
1.3	40	71	40/60	25 (1*R*,2*S*)	28 (1*R*,2*R*)
1.3	55	68	49/61	21 (1*R*,2*S*)	25 (1*R*,2*R*)
1.0	25	71	40/60	29 (1*R*,2*S*)	32 (1*R*,2*R*)
2.0	25	70	40/60	22 (1*R*,2*S*)	23 (1*R*,2*R*)
3.0	25	71	40/60	14 (1*R*,2*S*)	15 (1*R*,2*R*)

Finally, we have attempted to improve the stereoselectivity with ligands **1** and **4** by »double induction«, using esters of diazoacetic acid with (+) and (–) enantiomers of menthol. Again, no significant increase of enantioselectivity was observed (34% e.e. for *cis* isomer with ligand **1**), Table VII.

TABLE VII

Enantioselectivity of cyclopropanation of styrene with ethyl- or menthyl-diazoacetate

Ligand	R	Yield %	*cis/trans* %	*cis* (e.e. or d.e./%)	*trans* (e.e. or d.e./%)
1	Et	71	40/60	30 (1*R*,2*S*)	32 (1*R*,2*R*)
	(–) Mn	74	22/78	34 (1*R*,2*S*)	30 (1*R*,2*R*)
	(+) Mn	73	24/76	23 (1*R*,2*S*)	5 (1*R*,2*R*)
4	Et	71	38/62	14 (1*R*,2*S*)	7 (1*R*,2*R*)
	(–) Mn	73	26/74	16 (1*R*,2*S*)	2 (1*R*,2*R*)
	(+) Mn	74	18/82	10 (1*R*,2*S*)	8 (1*S*,2*S*)

CONCLUSION

Based on ^{1}H-NMR data (1D- and 2D-NMR, HETCOR, COSY and NOESY) as well as on MM2 calculations, configuration and conformation of bidentate nitrogen ligands **1–6** were determined. Cu(I) complexes of ligands **1–6** revealed low to medium selectivity in cyclopropanation of styrene. This outcome is rationalized by the energetically unfavourable interactions that prohibit formation of planar 5-membered chelate ring with ligands **1**, **4** and **6** required for effective enantioselection in cyclopropanation. Almoust double enantioselectivity obtained with the Cu(I) complex of **1** as compared to **6**, is explained by more restricted steric requirements, enhancing enantioface selection, in the former complex which possesses *gem* dimethyl group in the proximity of the chiral centre, near the coordination sphere of alkene and carbene.

EXPERIMENTAL

Melting points were determined on an Electrothermal Melting Point Apparatus 9100 in capillary tubes, and are uncorrected. NMR spectra were recorded in $CDCl_3$ on a Varian XL-300 GEM spectrometer using TMS as internal standard. IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer. Optical rotations were measured on a Optical Activity AA-10 Automatic Polarimeter in a 1 dm cell, concentrations are given in g/100 ml. The force field calculations were performed using standard procedure in SYBIL software package of TRIPOS Assoc.

General Procedure for the Preparation of Schiff Bases ***1–6***

The appropriate diamine (2.0 mmol), *R*-camphor or *R*-fenchone (4.0 mmol), and few crystals of *p*-toluenesulphonic acid, dissolved in toluene (30 ml), were heated under reflux and stirring for 70–120 hours. The apparatus was set up in the way that the vapours pass a side-arm connecting reaction vessel and reflux condenser, while the condensate returns passing through the glass tube filled with P_2O_5 on inert support.[10] After cooling to room temperature, the solution was poured off from the gummy residue, which was further extracted with dichlormethane. The combined organic layers were washed with water, dried over sodium sulphate, evaporated, and oily products purified by repeated bulb-to-bulb distillation *in vacuo* using the Büchi GKR-51 apparatus.

R-*1,2-(Bis-camphorimino)ethane* ***(1)***

Reaction time: 70 hours. Distillation (2 times, 225 °C/0.1 mmHg) yielded pure product as yellow oil, which crystallizes in refrigerator, m.p. 40 °C, yield 61%, $[\alpha]_D = -30.5$ ($c = 1.0$, CH_2Cl_2). IR(KBr) ν_{max}/cm^{-1}: 3420 (br), 2940, 1685 (C=N), 1440, 1380, 1365, 1320, 1285, 1270, 1195, 1025.

Anal. calcd. for $C_{22}H_{36}N_2$ ($M_r = 328.53$): C 80.42%, H 11.05%, N 8.53%. Found: C 80.46%, H 10.19%, N 8.74%.

R-*1,3-(Bis-camphorimino)propane* (**2**)

Reaction time: 95 hours. Distillation (2 times, 225 °C/0.3 mm Hg) yielded pure product as yellow oil, yield 33%, $[\alpha]_D = -43.0$ (c = 1.0, CH_2Cl_2). IR(KBr) ν_{max}/cm^{-1}: 3330, 2910 (br), 1685 (C=N), 1445, 1385, 1370, 1270,1195, 1100, 1050.

Anal. calcd. for $C_{23}H_{38}N_2$ (M_r = 342.55): C 80.70%, H 11.11%, N 8.19%. Found: C 80.47%, H 10.90%, N 8.23%.

R-*1,4-(Bis-camphorimino)butane* (**3**)

Reaction time: 120 hours. Distillation (3 times, 175 °C/0.08 mm Hg) yielded pure product as yellow oil, yield 24%, $[\alpha]_D = -29.0$ (c = 1.0, CH_2Cl_2). IR(KBr) ν_{max}/cm^{-1}: 3350 (br), 2910 (br), 1685 (C=N), 1445, 1390, 1370, 1275, 1260, 1200, 1105, 800.

Anal. calc. for $C_{24}H_{40}N_2$ (356.58): C 80.90%, H 11.23%, N 7.87%. Found: C 81.05%, H 11.44%, N 7.83%.

R-*1,2-(Bis-camphorimino)benzene* (**4**)

Reaction time: 120 hours. Distillation (2 times, 225–250 °C/0.1 mmHg) yielded pure product as yellow oil, which crystallizes in refrigerator, m.p. 128–131 °C, yield 28%, $[\alpha]_D = +57.5$ (c = 1.0, CH_2Cl_2). IR(KBr) ν_{max}/cm^{-1}: 3400 (br), 2945, 1680 (C=N), 1590, 1475, 1440, 1385, 1365, 1270, 1220, 1100, 1060, 760, 740, 710.

Anal. calcd. for $C_{26}H_{36}N_2$ (M_r = 376.57): C 82.98%, H 9.57%, N 7.45%. Found: C 82.79%, H 9.51%, N 7.59%.

R-*1,3-(Bis-camphorimino)benzene* (**5**)

Reaction time: 95 hours. Distillation (2 times, 200 °C/0.2 mm Hg) yielded pure product as yellow oil, yield 41.7%, $[\alpha]_D = +33$ (c = 1.0, CH_2Cl_2). IR(KBr) ν_{max}/cm^{-1}: 3420 (br), 2945, 1680 (C=N), 1590, 1570, 1470, 1440, 1385, 1365, 1270, 1060, 870, 790, 750, 710, 695.

Anal. calcd. for $C_{26}H_{36}N_2$ (M_r = 376.57): C 82.98%, H 9.57%, N 7.45%. Found: C 82.78%, H 9.53%, N 7.29%.

R-*(Bis-fenchoneimino)ethane* (**6**)

Reaction time: 120 hours. Distillation (2 times, 150–225 °C/0.2 mmHg) yielded pure product as yellow oil, which crystallizes in refrigerator, m.p. 52–55 °C, yield 38.4%, $[\alpha]_D = -46.3$ (c = 0.67, CH_2Cl_2). IR(KBr) ν_{max}/cm^{-1}: 3450 (br), 2970, 2880, 1685 (C=N), 1465, 1390, 1370, 1365, 1290, 1100, 1035.

Anal. calcd. for $C_{22}H_{36}N_2$ (M_r = 328.53): C 80.42%, H 11.05%, N 8.53%. Found: C 80.70%, H 10.95%, N 8.44%.

Catalytic Cyclopropanation

To the excess of styrene (0.52 g, 0.57 ml, 5.0 mmol) the precatalyst copper(I) trifluoromethanesulphonate benzene complex (15 mmol, available from »Fluka«) and 20 mmol of the chiral Schiff base were added. Afterwards, alkyl diazoacetate (1 mmol, *i.e.* 1 ml of the 1 M solution in 1,2-dichloroethane) was added dropwise by means of a syringe pump over a period of 4.5 hours. The reaction was carried overnight at room temperature with magnetic stirring under inert argon atmosphere. Diastereomeric mixture of *cis*/*trans* alkyl 2- phenylcyclopropan-1-carboxylates was isolated on silicagel column (1 × 15 cm) with ethylacetate – light petroleum (gradient

0–10%) as eluent. Diastereomeric composition and chemical yield were determined by gas chromatography on capillary column HP-1 (25 m × 0.25 mm I.D., »Hewlett Packard«) with biphenyl as an internal standard. Enantiomeric purity (e.e.) of ethyl esters was determined on a GLC chiral capillary column CP-Chirasil-DEX CB (25 m × 0.25 mm I.D., »Chrompack«), and diastereomeric purity of menthyl esters was determined on an achiral capillary column HP-1. The obtained e.e.'s are the average values of at least two experiments that differ by *ca.* ±1%.

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SAŽETAK

Strukturna svojstva odabranih C_2-simetričnih Schiffovih baza i stereoselektivnost njihovih Cu(I) kompleksa u reakciji ciklopropanacije

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Pripravljene su C_2-simetrične Schiffove baze (**1–6**) polazeći od *R*-kamfora odnosno *R*-fenhona kao izvora kiralnosti. Konfiguracija i konformacija pripravljenih spojeva određena je pomoću 1D- i 2D-NMR spektara, te dodatno potvrđena MM2 računima. Cu(I) kompleksi ovih spojeva pripravljeni *in situ* daju nisku do srednju enantioselektivnost (2–32%) u reakciji ciklopropanacije stirena. Korelacija struktura *E,E*-**1** i *Z,Z*-**6** i enantioselektivnosti njihovih Cu(I) kompleksa ukazuje na prostorne zahtjeve u *E,E*-**1**, koji posjeduje *gem* dimetil skupine u susjedstvu kiralnog centra u blizini koordinacijske sfere alkena i karbena, kao vjerojatni uzrok njegove više enantioselektivnosti.