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Asymmetric Hydrogen-Transfer Hydrogenation on Rhodium(I) Complexes with New Optically Active Salen Ligands Derived from (4*S*,5*S*)-4,5-Bis(aminomethyl)-2,2-dimethyl-1,3-dioxolane

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Abstract—New optically active C_2-symmetric salen-type ligands were synthesized on the basis of (4*S*,5*S*)-4,5-bis(aminomethyl)-2,2-dimethyl-1,3-dioxolane. These ligands were used to obtain cationic (trifluoromethanesulfonate) and neutral (chloride) rhodium(I) complexes with [(4*S*,5*S*)-2,2-dimethyl-5-{[(*E*)-pyridin-2-ylmethylidene]aminomethyl}-1,3-dioxolan-4-yl]-*N*-[(*E*)-pyridin-2-ylmethylidene]methanamine and [2,2-dimethyl-5-{[(*E*)-quinolin-2-ylmethylidene]aminomethyl}-1,3-dioxolan-4-yl]-*N*-[(*E*)-quinolin-2-ylmethylidene]methanamine. The latter complex ensured preparation of (*S*)-2-phenylethanol with an optical yield of 34.8% by transfer hydrogenation of acetophenone.

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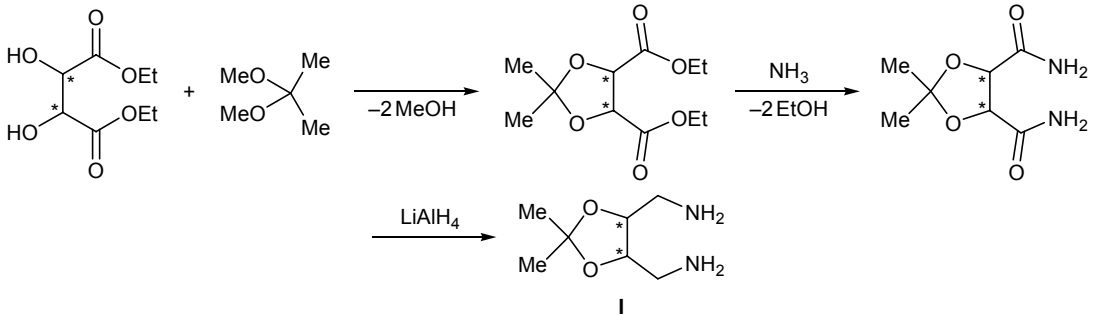
Transition metal complexes with Schiff bases (so-called *salen* complexes) in which the donor centers are oxygen and nitrogen atoms are extensively studied due to the possibility for controlling their steric and electronic properties via appropriate selection of primary mono- and diamine precursors and substituted aldehydes [1–6]. Chiral salen metal complexes effectively catalyze various processes. Catalytic asymmetric epoxidation and cyclopropanation reactions in the presence of Mn(III), Co(III), and Cr(III) salen complexes [2–6], including complexes intercalated into zeolite pores and macromolecules [7], were studied in most detail. Chiral C_2-symmetric salen ligands (and the corresponding metal complexes) obtained from optically active 1,2-diarylethane-1,2-diamines or cyclohexane-1,2-diamine were used most frequently [3, 8–10]. These complexes showed a high catalytic activity and moderate enantioselectivity (up to *ee* 73%) in borohydride reduction of aromatic ketones [11]. The use of rhodium salen complexes in the reduction of prochiral compounds was reported [1, 12].

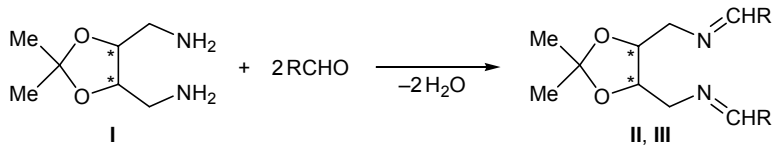
There are almost no published data on the synthesis of salen-type ligands and their metal complexes on the basis of other diamines than 1,2-diarylethane-1,2-diamines or cyclohexane-1,2-diamine. The known exception is chiral salen ligands derived from binaphthyldiamine; the corresponding complexes were used in the synthesis of cyclic carbonates [13]. Unlike amine ligands with sp^3-hybridized nitrogen atoms, nitrogen-containing salen ligands with sp^2-nitrogen atoms are softer bases which do not reduce the metal ion in the complex. Therefore, asymmetric transformations catalyzed by such complexes are expected to occur without reduction of the transition metal ion which often accompanies reactions in the presence of complexes with diamine ligands.

Taking the above stated into account, in continuation of our studies on enantioselective reduction in the presence of cobalt [14] and rhodium complexes [15–17] in the present work we synthesized novel *N*,*N*,*N*,*N*-salen ligands on the basis of (4*S*,5*S*)-4,5-bis-(aminomethyl)-2,2-dimethyl-1,3-dioxolane. As initial primary diamine we used (2*S*,3*S*)-3,4-isopropylidenedioxybutane-1,4-diamine (**I**) which was prepared according to Scheme 1 [16]. Optically active salen ligands **II** and **III** were synthesized in moderate yield by condensation of diamine **I** with pyridine-2-carbaldehyde and quinoline-2-carbaldehyde, respectively

Scheme 1.



Scheme 2.



II, R = pyridin-2-yl; **III**, R = quinolin-2-yl.

(Scheme 2). The structure of compounds **II** and **III** was confirmed by elemental analyses and spectral data. Rhodium(I) complexes with ligand **II** were obtained from neutral dinuclear complex $[(1,5\text{-COD})RhCl]_2$ (**IV**) and cationic trifluloromethanesulfonate complex $[(1,5\text{-COD})Rh]^+CF_3SO_3^-$ (**V**); the latter was prepared by treatment of **IV** with silver trifluoromethanesulfonate according to the procedure described in [17] (Scheme 3).

The structure of complexes **VI** and **VII** was analogous to the structure of manganese salen complexes [18] and was confirmed by IR and NMR spectroscopy. The IR spectrum of free ligand **II** contained an absorption band at 1650 cm^{-1}, which almost did not change its position on going to cationic complex **VII** (1648 cm^{-1}). This means that the double character of the C=N bond is retained as a result of opposite effects of coordination of the azomethine and pyridine nitrogen atoms to the metal ion. Table 1 shows chemical shifts of protons in compound **II** and complexes **VI** and **VII**. Complex **VII** demonstrates a strong upfield shift of the N=CH signal ($\Delta\delta$ = –1.07 ppm), an appreciable downfield shift of signals from 3-H and 4-H in the pyridine ring ($\Delta\delta$ = 0.34 and 0.29 ppm), and a weak upfield shift of the 5-H signal ($\Delta\delta$ = –0.07 ppm). Obviously, no such shifts of signals from protons in the heteroring would be observed in the absence of coordination of the pyridine nitrogen atom to the central metal ion. Moreover, in this case the CH=N proton signal would be shifted downfield rather than upfield.

Apart from compound **II**, we also synthesized ligand **III** containing bulkier quinoline fragments. We expected increased steric hindrances in the coordination sphere of Rh(I) in the corresponding complex at the stage of chirality transfer to the substrate, which

Scheme 3.

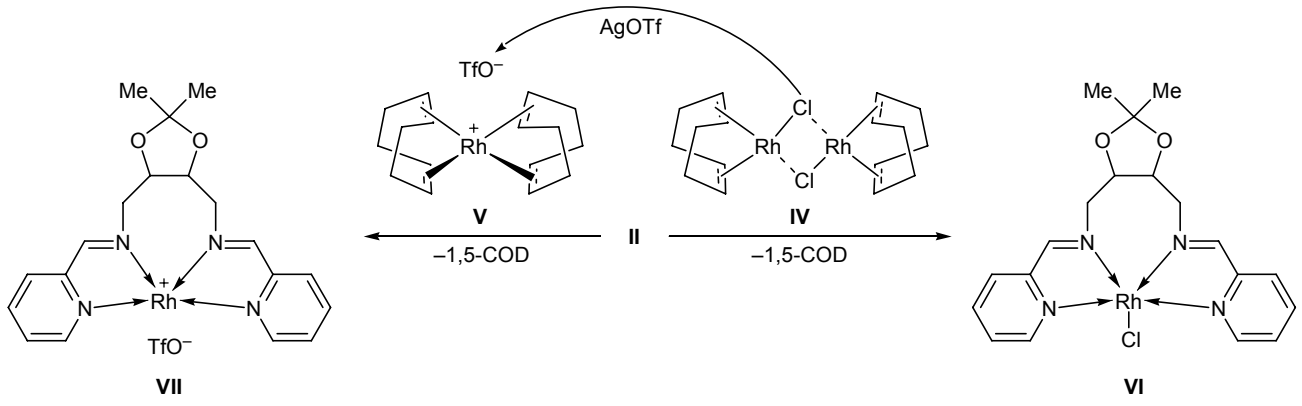


Table 1. Chemical shifts of protons (δ, ppm) in the ^{1}H NMR spectra of ligand **II** and rhodium complexes **VI** and **VII**

Compound no.	Solvent	CH_3	CH_2	CH	=CH	3-H	4-H	5-H	6-H
II	$CDCl_3$	1.41	3.96	4.36	8.44	8.02	7.73	7.30	8.64
VI	$CDCl_3$	1.43	3.46	3.74, 3.95	5.56	7.84 – 8.61			
VI	Acetone	1.31	3.90, 3.99	4.35	8.40	8.04	7.83	7.41	8.62
VII	Acetone	1.39	3.89, 3.72	4.32	7.34	8.38	8.12	7.34	8.63

should enhance enantioselectivity of the reduction process. According to the NMR and IR spectra, diimine **III** was isolated as individual substance. It was used in the transfer hydrogenation of acetophenone with propan-2-ol in the presence of neutral complex **IV** (Scheme 4).

Scheme 4.

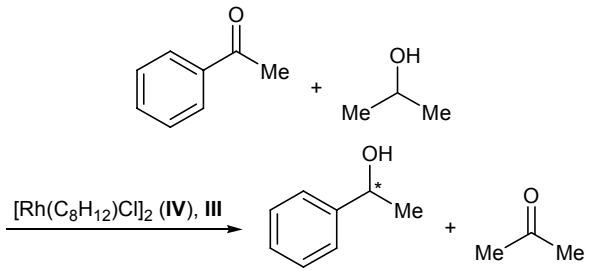


Figure shows the plot of concentration of acetophenone versus reaction time. Three parts of the kinetic curve can be distinguished. The first part is likely to correspond to hydrogenation of cyclooctadiene molecule and concurrent reaction involving complexes containing no cyclooctadiene. The next part reflects the highest activity of the system, and the third part corresponds to slow hydrogenation.

The results obtained in the presence of different catalysts are collected in Table 2. Salen complexes ensure higher conversion as compared to diamine rhodium(I) complexes [14]. Furthermore, no deposition of rhodium metal is observed in the reactions catalyzed by salen complexes. Complex **IV** with salen ligand **III** (which is more sterically hindered than ligand **II**) showed both higher asymmetric induction (enantioselectivity) in the transfer hydrogenation of acetophenone and higher catalytic activity as compared to **VI** and **VII** (31.5 and 7.0–8.0 mol of acetophenone per mole of Rh per hour).

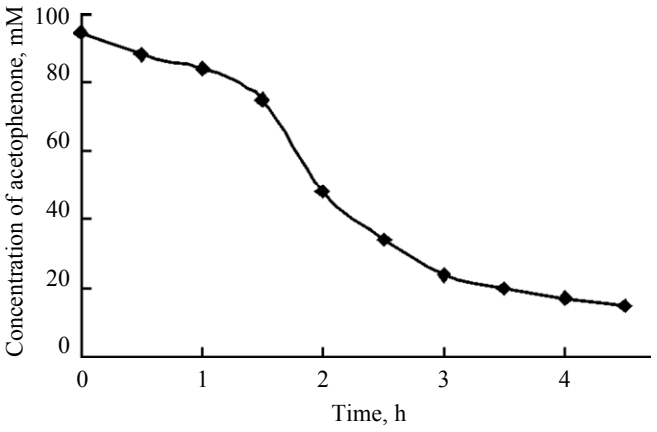
EXPERIMENTAL

Acetophenone and solvents (propan-2-ol, toluene) were thoroughly purified and dehydrated and were stored under argon. All reactions were carried out in an argon atmosphere.

The IR spectra were recorded in KBr on an IKS 29 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX 400 spectrometer at 400 (^{1}H) and 100 MHz (^{13}C) using hexamethyldisiloxane as internal reference (the chemical shifts are given relative to tetramethylsilane). GLC analysis was performed on an LKhM 80 chromatograph equipped with a thermal conductivity detector (2000×3-mm column packed with 5% of SE-30 on Chromaton N-AW-DMCS; carrier gas helium) and on a Shimadzu QP2010 Plus GC–MS system (electron impact, 70 eV, a.m.u. range from 40 to 350; Equity 5 capillary column, 30 m×0.25 mm, 95% of dimethylpolysiloxane and 5% of diphenylpolysiloxane; carrier gas helium; oven temperature programming from 110 to 250°C, injector temperature 250°C, interface and ion source temperature 200°C). The mass spectra corresponding to the apices of chromatographic peaks were compared with reference spectra in the NIST05 library. The optical rotations were measured on an ADP410 automatic digital polarimeter at λ 589 nm (cell path length 50 mm, concentration 2–30 g/100 ml, solvent metha-

Table 2. Transfer hydrogenation of acetophenone on Rh(I) complexes (solvent propan-2-ol, base KOH, 78°C)

Complex	c_{Rh}, mM	$c_{PhC(O)Me}/c_{Rh}$	Time, min	Conversion, %	r_{max}, mmol l^{-1} h^{-1}	Maximal activity, mol of PhC(O)Me per mole of Rh per hour	*ee*, %
VI	1.7	80	540	79.8	13.4	8.0	0.9 (*S*)
VII	1.6	86	525	23	7.9	5.0	6.7 (*S*)
VII	1.1	86	535	68	7.7	7.0	2.5 (*S*)
IV + **III**	1.1	86	270	84	34.7	31.5	34.8 (*S*)



Plot of acetophenone concentration in propan-2-ol versus time in the transfer hydrogenation using the system $[Rh(COD)Cl]_2$–**III**; c_{Rh} = 1.1 mM, [**III**] : [Rh] = 3, 75°C.

nol). The optical yields were calculated with respect to the specific rotation of (*S*)-(–)-1-phenylethanol ([α] = –45.0°, *c* = 5, MeOH) [19].

(4*S*,5*S*)-(2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis-{*N*-[(1*Z*)-pyridin-2-ylmethylidene]methanamine} (II). (4*S*,5*S*)-4,5-Bis(aminomethyl)-2,2-dimethyl-1,3-dioxolane (**I**) ($[\alpha]_D$ = –8.17°, *c* = 8.7, PhH), 0.016 mol (0.8 g), was dissolved under stirring in 30 ml of methanol, the solution was heated to the boiling point, and a solution of 0.032 mol (1.126 g) of pyridine-2-carbaldehyde in 20 ml of methanol was added dropwise over a period of 30–40 min. The mixture was stirred for 2 h and left overnight, and the light brown precipitate (large crystals) was filtered off, washed with hexane, and dried. Yield 86%, mp 92–95°C, $[\alpha]_{546}^{25}$ = –6.7° (*c* = 0.80, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1650, 1580, 1565. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 s (3H, CH_3), 3.92 d.d (1H, CH_2, *J* = 12.5, 3.7 Hz), 3.99 d.d (1H, CH_2, *J* = 12.5, 2.4 Hz), 7.30 m (1H, 5-H), 7.73 d.d (1H, 4-H, *J* = 7.6, 1.0 Hz), 8.02 d (1H, 3-H, *J* = 7.8 Hz), 8.44 s (1H, N=CH), 8.64 d (1H, 6-H, *J* = 4.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.22 (CH_3), 63.10 (CH_2), 78.56 (OCH), 109.43 (OCO), 121.30 (C^3), 124.80 (C^5), 136.47 (C^4), 149.38 (C^6), 154.33 (C^2), 164.09 (N=CH). Found, %: C 67.11; H 6.65; N 16.67. $C_{19}H_{22}N_4O_2$. Calculated, %: C 67.44; H 6.55; N 16.56.

([2,2-Dimethyl-5-{[(*E*)-quinolin-2-ylmethylidene]aminomethyl}-1,3-dioxolan-4-yl]-*N*-[(*E*)-quinolin-2-ylmethylidene]methanamine) (III). Compound **I**, 0.016 mol (2.57 g), was dissolved under stirring in 40 ml of methanol, the solution was heated to the boiling point, and a solution of 0.040 mol (6.28 g) of quinoline-2-carbaldehyde in 30 ml of methanol was added dropwise over a period of 40–50 min. The resulting brown solution was heated for 2 h under reflux with stirring, cooled, and left overnight. The light brown precipitate was filtered off, washed with diethyl ether, and dried under reduced pressure. Yield 18%, mp 114–115°C, $[\alpha]_D$ = –8.17° (*c* = 8.7, C_6H_6). IR spectrum, ν, cm^{-1}: 1646, 1597, 1561. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.45 s (3H, CH_3), 4.05 m (2H, CH_2), 4.45 m (1H, OCH), 7.58 t (1H, 6-H, *J* = 7.3 Hz), 7.75 t (1H, 7-H, *J* = 7.6 Hz), 7.83 d (1H, 5-H, *J* = 7.9 Hz), 8.12 d (1H, 8-H, *J* = 8.4 Hz), 8.17 m (1H, 3-H, 4-H), 8.62 s (1H, N=CH). Found, %: C 74.11; H 6.05; N 12.67. $C_{27}H_{26}N_4O_2$. Calculated, %: C 73.95; H 5.98; N 12.78.

([2,2-Dimethyl-5-{[(*E*)-pyridin-2-ylmethylidene]aminomethyl}-1,3-dioxolan-4-yl]-*N*-[(*E*)-pyridin-2-ylmethylidene]methanamine)rhodium(I) chloride (VII). A test tube was charged in a stream of argon with 0.1 mmol (49.3 mg) of $[Rh(COD)Cl]_2$, 10 ml of THF was added, and the mixture was stirred until complete dissolution. A solution of 0.2 mmol (67.6 mg) of compound **II** in a small amount of THF was then added, and the blue–violet solution was stirred for 24 h and evaporated to a volume of 3 ml. The blue–violet precipitate was washed with several small portions of diethyl ether and dried under reduced pressure. Yield 0.09 g (95%). IR spectrum, ν, cm^{-1}: 1648, 1590, 1567. The ^1H NMR spectrum is given in Table 1.

([2,2-Dimethyl-5-{[(*E*)-pyridin-2-ylmethylidene]aminomethyl}-1,3-dioxolan-4-yl]-*N*-[(*E*)-pyridin-2-ylmethylidene]methanamine)rhodium(I) trifluoromethanesulfonate (VII). A test tube was charged in a stream of argon with 0.1 mmol (49.3 mg) of $[Rh(COD)Cl]_2$, 10 ml of THF was added, and the mixture was stirred until complete dissolution. A solution of 0.2 mmol (51.4 mg) of silver trifluoromethanesulfonate in 20 ml of THF was added, and the mixture was stirred for 30 min. The precipitate was filtered off through a layer of silica gel and washed on a filter with several small portions of THF. A solution of 0.2 mmol (67.6 mg) of compound **II** in a small volume of THF was added, and the resulting dark red solution was stirred for 24 h and evaporated to a volume of 3 ml. The dark red precipitate was washed with several portions of diethyl ether and dried under reduced pressure. Yield 112 mg (95%). IR spectrum, ν, cm^{-1}: 1648, 1638, 1597. The ^1H NMR spectrum is given in Table 1.

Transfer hydrogenation of acetophenone with propan-2-ol. A vessel was charged in a stream of argon with 0.025 mmol (12.4 mg) of dinuclear rhodium complex $[Rh(COD)Cl]_2$ and 45 ml of propan-

2-ol. Compound **III**, 0.05 mmol (22.1 mg), was added to the bright yellow solution which immediately turned brown, 0.2 ml of hexadecane (internal standard) and 0.15 mmol (8.4 mg) of KOH (co-catalyst) were added, the mixture was stirred for 15 min, 4.3 mmol (0.5 ml) of acetophenone was added, and the mixture was stirred for 5 min and maintained at 75°C. Samples for GLC analysis were taken every 30 min.

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