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Rhodium(I) Bisaldimine Complexes in Transfer Hydrogenation

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Abstract—The reactions of hydrogen transfer from 2-propanol on acetophenone in the presence of the system $[Rh(cod)Cl]_2$–L] (L is bisaldimine ligands based on (*R,R*)-1,2-cyclohexanediimine and pyridine-, quinoline-, and thiophenecarboxaldehyde) were studied. Rhodium(I) complexes with optically active ligand showed a high catalytic activity (up to 345 h^{-1}) and moderate enantioselectivity [up to 55% *ee* of (*R*)-1-phenyethanol]. The structure of rhodium complex with *N,N'*-(1*R*,2*R*)-cyclohexane-1,2-diyl-bis[1-(pyridine-2-yl)methanimine] was determined on the basis of the data of ^1H and ^{13}C NMR spectroscopy and quantum chemical calculations.

Keywords: rhodium, bisaldimine ligands, hydrogen transfer, acetophenone

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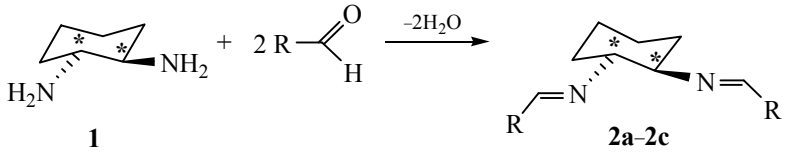
Growing interest to the use of optically active secondary alcohols in pharmaceutical chemistry stimulated intensive development of the methods of asymmetric reduction of prochiral aromatic ketones including asymmetric hydrogenation of C=O bonds with hydrogen transfer from its sources in the presence of ruthenium(II), rhodium(I), and iridium(I) complexes containing chiral bipyridines [1–3], alkylphenanthrolines [4], diimines [5–8], diamines [8–10], ureas, and thioureas [11].

In recent decades attention of researchers was focused on the synthesis and application of optically active chiral ligands based on diamines and amino alcohols, which, like the phosphine ligands, are not easily oxidized in the transition metal coordination sphere and at the same time retain high stereogenic ability. Usually chiral *N,N*-ligands act as bidentate donors [2, 12–16]. In particular, it is known that ruthenium complexes containing (*R,R*)- and (*S,S*)-*N*-(toluenesulfonyl)-1,2-diphenyl-diaminoethane as ligands are highly efficient in the asymmetric reduction of arylketones in both 2-propanol and in a mixture of formic acid with triethylamine [17, 18]. The disadvantage of chiral diamines is a comparatively low catalytic activity of their complexes with transition metals in transfer hydrogenation reactions and in transition metal reduction to the elemental state, which has occurred in some cases [9, 19].

Published data on the effectiveness of optically active *N,N*- or *N,N,N,N*-rhodium complexes, in which nitrogen atoms are in the sp^2-hybridization state, in acetophenone transfer hydrogenation are highly scattered. For example, enantioselectivity for $[CpRhCl_2]_2$ is reported to be from 12% *ee* with the ligand (*R*)-pyridyl-3-*i*-propyloxazoline up to 51% *ee* with the ligand (*R*)-2-pyridynal-l-phenylethylimine [20]. The *ee* value of 48% of (*S*)-1-phenyethanol was obtained with the ligand (*R,R*)-1,2-dibenzylidene 1,2-cyclohexanediimine on the dimeric complex $[Rh(1,5\text{-cod})\mu\text{-Cl}]_2$ [7]. Iridium(I) and ruthenium(II) complexes with sp^2-nitrogen bi- and tetradentate ligands [21, 22] also do not permit high *ee* values to be reached with sp^3-nitrogen ligands [17, 18].

It seems interesting to use ligands with chemilabile donor functions that can take potentially vacant coordination sites at metal centers in intermediates and freed them when necessary for coordination of substrates under conversion. Although functionalized phosphines containing *O*- and *N*-donor fragments and *N,H,C*-functionalized ligands [23–24] are the most studied hemilabile ligands, also *N,N,N,N*- and *S,N,N,S*-tetradentate ligands containing heteroatoms with

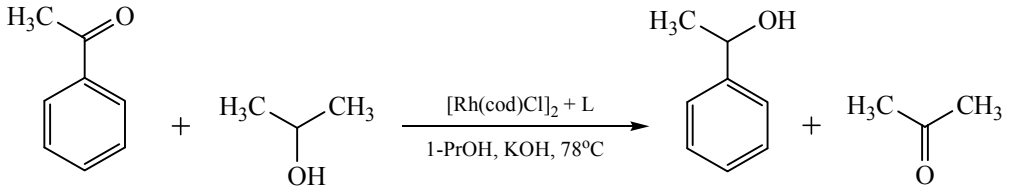
Scheme 1.



1 **2a–2c**

R= 2-pyridyl (**a**), 2-quinolyl (**b**), 2-thienyl (**c**).

Scheme 2.



various coordinating properties may be of interest in obtaining new systems applicable in homogeneous catalysis [25–30].

The aim of this work was to test rhodium(1+) complexes with bis-aldimine ligands, generated *in situ,* in hydrogen transfer of acetophenone and to determine composition and structure of the rhodium complex with *N,N′*-[(1*R,*2*R*)-cyclohexane-1,2-diyl]bis[1-(pyridine-2-yl)]methanimine.

Bis-diimine ligands **2a–2c** (Scheme 1) were synthesized by the reaction of diamine **1** with aldehydes containing a dentate heteroatom in the α-position (2-pyridinecarboxaldehyde, 2-quinolinecarboxaldehyde, and 2-thiophenecarboxaldehyde).

The active reaction catalyst is formed *in situ* when the dimeric complex [Rh(1,5-cod)μ-Cl]$_2$ interacts with a small excess of optically active *N,N,N,N*-ligands in a solution of 2-propanol in the pre-sence of potassium *tert*-butylate or KOH (Scheme 2). The reaction was studied in the concentration ranges of acetophenone (1.9–19)×10^{-2} M, rhodium (3–22)×10^{-4} M, and 1-phenyethanol (6–10)×10^{-2} M.

It may be noted that the ketone transfer hydrogenation in the presence of the catalyst with ligand **2a** occurs at a high rate. For example, in the case of 0.5 mL (4.3 mmol) of acetophenone in the presence of 1 mol % of the catalyst 95–96% acetophenone transformation to 1-phenylethanol is reached within 1 h, TOF$_{ini}$ 345 h^{-1}, no by-products are formed. In most cases (*R*)-1-phenylethanol is presumably formed, and only with ligand **2b** excess of (*S*)-isomer is formed.

Enantioselectivity of the catalytic reaction grows in the series of the ligands: **2a** < **2b** < **2c** (Table 1, exp. nos. 7, 16, and 17). In the same order TOF for rhodium catalysts decreases. When the reaction product *rac*-1-phenylethanol (47.6 mmol/L, 1/2 of the initial ketone concentration) is initially introduced in the reaction mixture, the reaction rate and enantioselectivity are slightly reduced (exp. nos. 5 and 14), whereas a significant W_{ini} reduction appears even at the concentration equal to 1/4 of the initial acetophenone concentration. If the reaction product, acetone, was introduced at the beginning of the reaction, the enantiomer excess of (*R*)-1-phenylethanol increases (compare, for example, exp. nos. 4 and 15).

The bidentate coordination of *N,N,N,N*-ligands is possible in rhodium cyclooctadiene complexes. To determine the structure of forming complexes, we have studied the reaction of [Rh(COD)Cl]$_2$ with ligand **2a** by the methods of ^{1}H and ^{13}C NMR spectroscopy (Table 2). At –10°C in 10 min after the addition of ligand **2a** to a [Rh(cod)Cl]$_2$ solution new signals appear, which indicate that the bisaldimine ligand is coordinated to rhodium(I) (Table 2, exp. no. 2). The position and distribution of intensities of these signals in the spectrum of C^2-symmetric ligand bound in a complex indicate that they are magnetically nonequivalent. So, one of protons of the azomethine fragment undergoes the strongest downfield shift (Δδ = 1.13 ppm), resonance signals of methine protons at the carbon atoms C^1 (3.30 ppm, Δδ = –0.21 ppm) and C^2 (3.63 ppm, Δδ = 0.15) of the cyclohexane ring, and chemical shifts of protons at C$^{11,11'}$ and C$^{12,\ 12'}$ atoms in the pyridine fragments of the diimine ligand become nonequivalent.

Parameters of proton signals of the cyclooctadiene ligand in the complex Rh(cod)(**2a**)Cl, **3a,** indicate that the molecule remains bound with the rhodium(+1) central atom (Table 3). The ^{1}H NMR spectrum of the rhodium complex contains three signal from four vinyl protons of cyclooctadiene in the ratio of integral intensities of 1 : 1 : 2 at $\delta \approx 4.36$, 4.73, and 4.79 ppm, respectively, whereas the spectrum of the initial biscyclooctadiene chloride complex $[Rh(cod)Cl]_2$ contains only one resonance signal. A down-field shift of signals from vinyl protons and approacing of positions of resonances from CH_A and CH_B protons in the coordinated cyclooctadiene were observed when the triphenylphosphine molecule was coordinated to the rhodium complex $[Rh(cod)_2]^+CF_3SO_3^-$ [31].

Nonsymmetrical ligand coordination to rhodium in the complex is confirmed by the $^{13}C\{^1H\}$ NMR spectra. Thus, only carbon atoms C^4 and C^5 in the cyclohexane fragment of ligand **1a** are equivalent, whereas signals of the pairs of atoms C^3 (35.7 ppm), C^6 (32.6 ppm), and C^1 (53.1 ppm), C^2 (66.5 ppm), as well as resonance signals of carbon atoms in azomethine fragments ($\delta_{N=\underline{C}H}$ 154.5 ppm; $\delta_{N=\underline{C}H}$ 173.1 ppm) differ significantly. Ten carbon atoms in two pyridine fragments of the coordinated ligand and vinyl carbon atoms in the cyclooctadiene molecule are also nonequivalent: 121.6 (C^{11}) 126.1 ($C^{11'}$), 129.5 (C^9), 130.4 ($C^{9'}$), 137.6 (C^{10}), 141.7 ($C^{10'}$), 149.6 (C^{12}), 155.9 ($C^{12'}$), 150.6 (C^8), 162.1 ($C^{8'}$), 73.8 (2C, cod-CH_{vinyl}), 81.0 (2C', cod-CH_{vinyl}).

To reveal catalytic activity of the catalyst under study it is necessary to add bases to the reaction mixture.

$$Rh(cod)(\mathbf{2a})Cl + KO\text{-}i\text{Pr} = Rh(cod)(\mathbf{2a})O\text{-}i\text{Pr}(\mathbf{4}) + KCl. \quad (1)$$

In the absence of the substrate the hydrogenation of coordinated 1,5-cyclooctadiene occurs: signals of protons of products of hydrogen transfer on a coordinated diene, namely of free cyclooctene (2.29 and 5.42 ppm), cyclooctane (1.47 ppm), and acetone (2.10 ppm) appear in the spectrum. When KOH and acetophenone are introduced into the reaction mixture the hydrogenation of this latter is accompanied by the appearance of signals of 1-phenylethanol [2.5 (CH_3), 3.93 ppm (CH)] and acetone [1.99 ppm (CH_3)] along with cyclooctene and cyclooctane signals (Table 2, Scheme 3).

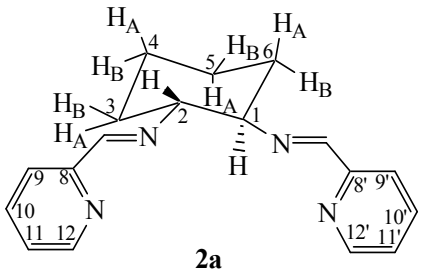
Product **4** of the reaction of complex **3a** with KOH was isolated from the reaction mixture (parameters of the ^{1}H NMR spectrum in $CDCl_3$ are shown in Tables 2 and 3). Ligand **2a** in the structure of rhodium isopropoxide complex **4** is also coordinated asymmetrically: protons of hydrogen atoms N–$C^{1,2}$H, $C^{10,10'}$H, $C^{12,12'}$H, and N=CH and vinyl protons in the diene molecule are not equivalent. Resonances of protons of the isopropoxide substituent at rhodium appear as a multiplet at 3.52 ppm (CH) and a broadened doublet at ~0.88 ppm (CH_3).

Table 1. Hydrogen transfer from 2-propanol on acetophenone in the presence of the system $[Rh(cod)Cl]_2$–**2**[a]

Exp. no.	Ligand	Acetophenone/Rh	$W_{acetophenone}$, mmol L^{-1} h^{-1}	TOF, h^{-1}	*ee*, % (R)
1[b]	**2a**	310	60±4.2	200±12.2	31±1.5
2	**2a**	35	17±1.0	31±1.8	35±1.7
3	**2a**	86	39±2.0	65±3.2	28±1.3
5	**2a**	260	108±5.5	196±9.8	32±1.6
6	**2a**	346	155±7.6	236±12.6	30±1.5
4	**2a**	155	68±3.4	110±6.6	37±1.7
8[c]	**2a**	86	378±18.6	345±12.6	26±1.1
9[d]	**2a**	86	438±21.2	197±9.7	35±1.6
10[e]	**2a**	172	58±2.7	113±6.6	28±1.4
11[f]	**2a**	172	24.0±1.3	65±3.8	32±1.5
12[g]	**2a**	172	11.0±0.4	19±1.1	17±0.8
13[d]	**2a**	86	548±23.1	248±12.3	32±1.6
14[h]	**2a**	172	71±3.2	129±6.4	32±1.6
15[i]	**2a**	172	24±1.1	44±2.6	49±2.5
16	**2b**	172	74±3.4	133±7.0	38±1.8 (*S*)
17	**2c**	172	11±0.6	20±1.1	43±2.3
18	**2d**	172	70±3.7	122±6.8	35±2.5
19[d,j]	**2a**	43	37±1.8	16±1.0	53±2.5
20[k]	**2a**	20	–	–	51

[a] $c_{acetophenone}$ = 95.2 mmol/L (172), c_{Rh} = 0.55 mmol/L, 78°C; *t*-BuOK or KOH, 2-propanol, toluene. [b] c_{Rh} = 0.3 mmol/L. [c] c_{Rh} = 1.1 mmol/L. [d] c_{Rh} = 2.2 mmol/L. [e] 60°C. [f] 50°C. [g] 30°C. [h] 47.3 mmol of 1-phenylethanol added. [i] 23.6 mmol of acetone added. [j] Substrate was added after complete 1,5-cyclooctadiene hydrogenation. [k] $[Cp\text{-}RhCl_2]_2$–HCO_2H/HCO_2Na, pH = 3.5, H_2O, 40°C [30].

Table 2. Parameters of ^{1}H NMR spectra of ligand **2a** and complex Rh(cod)(**2a**)Cl in 1-propanole at –10°C



2a

Comp. no.	δ, ppm (Δδ)							
	$C^{4,5}H_A$	$C^{4,5}H_B$ + $C^{3,6}H_AH_B$	$NC^{1,2}H$	$C^{11,11'}H$	$C^{10,10'}H$	$C^{9,9'}H$	N=CH	$C^{12,12'}H$
2a	1.50 m	1.80 m	3.51 br.s	7.35 d.d (*J* 4.5 Hz)	7.75 t (*J* 7.8 Hz)	7.99 d (*J* 7.8 Hz)	8.28 s	8.45 d (*J* 4.5 Hz)
3a (–10°C)	1.68 s (2H) (0.18)	2.02 m (6H) (0.22)	3.30 m (1H) (–0.20) 3.63 m (1H) (0.12)	7.48 t (1H, *J* 6.0 Hz) (0.13) 7.80 t (1H, *J* 6.0 Hz) (0.45)	7.98 t (2H, *J* 7.7 Hz) (0.22)	8.18 d (2H, *J* 7.7 Hz) (0.19)	8.40 s (1H) (0.12) 9.41 s (1H) (1.13)	8.57 d (1H, *J* 4.5 Hz) (0.12) 8.36 d (1H, *J* 7.7 Hz) (–0.09)
+KOH	1.64 m	1.79 m 2.10 s (acetone)	3.36–3.52 m	7.44 br.t (*J* 7.2 Hz)	7.86 br.t (*J* 7.8 Hz)	8.25 d (*J* 8.2 Hz)	8.46 br.s	8.46 br.s
4, $CDCl_3$	1.68 br.s	1.84 br.s	3.64 m (1H) 3.78 m (1H)	7.62 br.s	7.72 t (*J* 7.5 Hz) 7.79 t (*J* 7.5 Hz)	7.39 d (*J* 4.5 Hz)	8.30 s 8.58 s	7.92 d (*J* 7.5 Hz) 8.19 d (*J* 7.5 Hz)
4, Rh–O–*i*Pr	0.88 br.d(CH_3, *J* 6.3 Hz)		3.52 m (CH)					

Table 3. Parameters of ^{1}H NMR spectra of 1,5-cod in complexes $[Rh(cod)Cl]_2$ and Rh(cod)(**2a**)Cl in 1-propanol

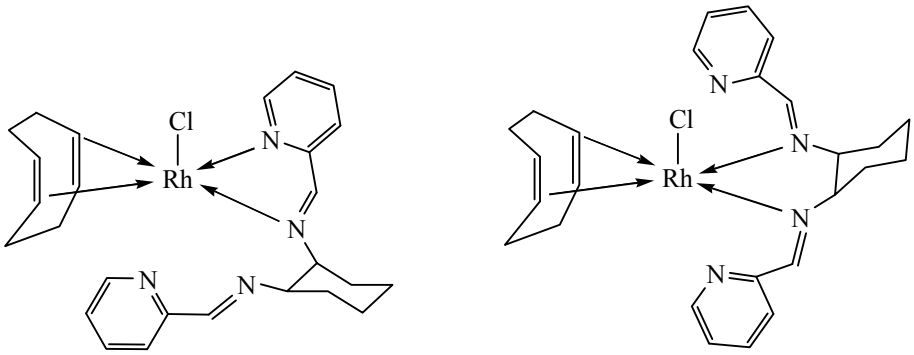
Complex	δ, ppm (Δδ)		
	CH	$C\underline{H}_ACH_B$	$CH_AC\underline{H}_B$
$[Rh(cod)Cl]_2$	4.36 m (4H)	2.50 m (4H)	1.77 m (4H)
Rh(cod)(**2a**)Cl (**3a**)	4.36 m (1H) (0.0), 4.73 m (1H) (0.37), 4.79 m (2H) (0.43)	2.33 m (4H) (–0.17)	2.02 m (4H) (0.25)
4 (**3a** + KOH), 60°C	4.50 m (2H) (0.14)[a], 4.63 m (2H) (–0.10), 5.42 m (2H, cyclooctene)	2.47 m (4H) (0.14),[a] 2.29 (12H, cyclooctene)	1.85 m (4H) (–0.17)[a]

[a] In relation to signals in complex **3a**.

It can be assumed that binding of bisaldimine ligand **2a** with rhodium central atom takes place through one pyridine and one aldimine nitrogen **3a** or, in the case of symmetrical *N,N*-coordination of nitrogen atoms, protons are not equivalent in pyridine fragments (**3b**). Inequality of protons in two halves of coordinated ligand **2a** (Fig. 1) can take place in both cases.

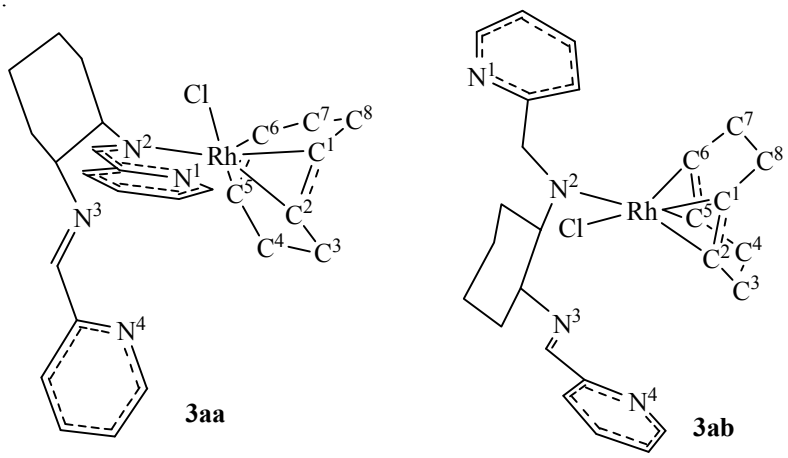
To refine the complex geometry, we have carried out calculations of rhodium complexes using the B3LYP hybrid functional on the software package Firefly version 8.1 [32]. Quantum chemical calculations with the use of the Lanl2dz basis set for rhodium atom and 6-31(G)(d) for other atoms confirm the formation of slightly distorted square-planar 18-electron rhodium(I) complex with **3aa**-type bidentate

Scheme 3.



3a **3b**

Scheme 4.



3aa **3ab**

coordination, in which a 1,5-cyclooctadiene molecule has the η^4-coordination and ligand **2a** is bound with the central atom through nitrogen atoms of one aldimine and one pyridine fragments. The 16-electron Rh(I) complex **3ab** is slightly more preferable in energy ($\Delta\Delta G^0$ = –0807 kcal/mol)**.** The corresponding constant of the equilibrium **3aa**↔**3ab** is equal to four, which corresponds to the 20% content of complex **3aa** in the equilibrium mixture. Some bond lengths and angles in complexes **3aa** and **3ab** are shown in Table 4.

Optimized geometry of complex **3ab** is a distorted planar square. Steric repulsion between pyridine fragment of ligand **2a** and cyclooctadiene molecule inhibits the interaction of the nitrogen atom in non-coordinated azomethine fragment with rhodium atom. It is probably 16-electron complex **3ab** which reacts with iPrOK to form compound **4**. The chiral ligand monodentate coordination is consistent with the data of the ^{1}H and ^{13}C NMR spectroscopy monitoring of its interaction with dimeric chloride complex $[Rh(cod)Cl]_2$ (Scheme 4).

To refine the sequence of the C=O bond hydrogenation in acetophenone and of double bonds in 1,5-cyclooctadiene, we monitored time changes of concentrations of cyclooctadiene contained in the complex [Rh(cod) (**2a**)Cl] and in a substrate. Kinetic curves of their hydrogenation in the same experiment are shown in Figs. 1 and 2. It can be seen that to the moment of almost complete acetophenone hydrogenation (τ 90 min, Fig. 1) 35% of initial 1,5-cyclooctadiene and 65% of cyclooctene (Fig. 2) remain in the system, and full cyclooctadiene hydrogenation to cyclooctane occurs within 17 h. Hence it follows that the reaction of acetophenone transfer hydrogenation is catalyzed by rhodium(I) cyclooctadiene and cyclooctene complexes, at least initially. In this experiment *ee* value for the *R*-isomer was 32%.

It should be noted that the introduction of the substrate in the reaction solution after complete 1,5-cyclooctadiene hydrogenation leads to an increase in the enantioselectivity of the process from 35 to 53 *ee* of (*R*)-1-phenylethanol (Table 1, exp. no. 19). Probably

Table 4. Several bond lengths and angles between bonds in complexes **3aa** and **3ab**

Bond	*d*, Å		Angle	φ, deg	
	3aa	**3ab**		**3aa**	**3ab**
Rh–Cl	2.643(80)	2.4476(6)	N^1RhCl	87.12(8)	
Rh–N^1	2.135(69)		N^1RhC^1	99.52(3)	
Rh–N^2	2.162(28)	2.181(63)	N^1RhC^2	92.54(6)	
Rh–C^1	2.155(23)	2.151(80)	N^1RhC^5	141.12(9)	
Rh–C^2	2.196(01)	2.184(63)	N^1RhC^6	178.49(6)	
Rh–C^5	2.178(31)	2.170(10)	$ClRhC^1$	87.38(1)	89.90(7)
Rh–C^6	2.157(73)	2.197(18)	$ClRhC^2$	124.26(0)	89.55(0)
			$ClRhC^5$	128.83(3)	166.62(0)
			$ClRhC^6$	93.23(1)	154.53(0)
			N^2RhCl	84.19(3)	88.74(5)
			N^2RhC^1	171.05(3)	162.94(8)
			N^2RhC^2	149.60(0)	159.58(1)
			N^2RhC^5	90.92(7)	96.32(1)
			N^2RhC^6	101.48(7)	92.71(3)

after the cyclic diene molecule departure from rhodium(I) coordination sphere the tetradentate coordination of the *N,N,N,N*-ligand takes place, and stereocontrol in diastereomeric transition states increases. According to NMR spectroscopy data, azomethine bonds in the ligand are not reduced in the process of the acetophenone transfer hydrogenation. The application of diamine ligand **2d** obtained by the diimine **2a** reduction with sodium tetrahydroborate leads to the *in situ* formation of a rhodium(I) complex, which is also active in transfer hydrogenation with a relatively high TOF and *ee* 35% for (*R*)-1-phenylethanol (Table 1, exp. no. 18).

Thus, the rate of the catalytic reaction of the diene transfer hydrogenation is significantly lower than that of the ketone, therefore the catalysis occurs on the rhodium(I) cyclooctadiene complexes with *N,N*'-(1*R,*2*R*)-cyclohexane–1.2-diyl-bis[1-(pyridine-2-yl)-methanimine] **2a**. The presence of such a strong ligand as 1,5-cyclooctadiene in the transition metal coordination sphere prevents tetradentate coordination of the *N,N,N,N*-ligand, which becomes possible only after complete diene hydrogenation. In the absence of a cyclooctadiene molecule from the metal coordination sphere an increase in the product *ee* is observed.

The stage of rhodium hydride formation from the rhodium isopropoxide complex Rh(cod)(**2a**)O-*i*Pr requires a free coordination site, which appears either on the hydration of one double bond in the diene or on the dissociation of the Rh–N bond that involves changing the geometric structure of the complex and also the concomitant from 2 to 1 in denticity of the *N,N,N,N*-ligand in the complex. This decrease, in turn, leads to a decrease in the degree of enantioface differentiation of the prochiral ketone molecule in the stage of chirality transfer. Thus, from the viewpoint of enantioselectivity value of the acetophenone transfer hydrogenation process, the presence of the cycloctadiene ligand in the coordination sphere of the rhodium(1+) complex is undesirable.

EXPERIMENTAL

Solvents and reagents [acetophenone, *R,R*-1,2-cyclohexane diamine, 2-pyridinecarboxaldehyde, 2-quinolinecarboxaldehyde (Aldrich)] used in this study were thoroughly purified, dehydrated according to known procedures [33], and stored in an argon atmosphere. All syntheses were also carried out in argon.

Elemental analysis was carried out on a Euro EA3000-Single instrument with argon as a carrier gas,

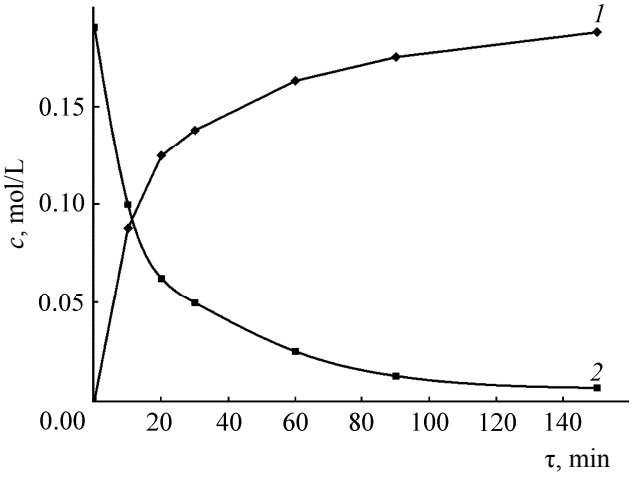


Fig. 1. Transfer hydrogenation of acetophenone ($c_{acetophenone}$ = 190.4 mmol/L, c_{Rh} = 2.22 mmol/L); (*1*) acetophenone and (*2*) 1-phenylethanol.

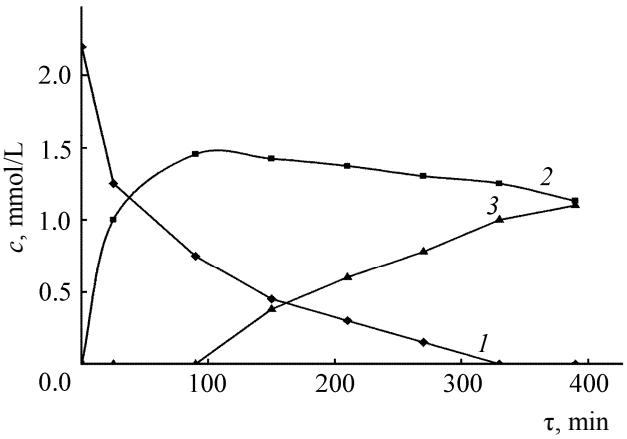


Fig. 2. Kinetic curves of 1,5-cyclooctadiene transfer hydrogenation on the complex Rh(cod)(**2a**)Cl (c_{Rh} = $c_{cyclooctadiene}$ = 2.22 mmol/L); (*1*) 1,5-cyclooctadiene, (*2*) cyclooctene, and (*3*) cyclooctane.

120 kPa, front oven temperature 980°C, and chromatograph thermostat temperature 100°C. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX250 pulse spectrometer at 298 K using a BBO5mmZ3074/58 broadband sensor, internal reference HMDS**.** Concentrations of solutions for recording ^{1}H NMR spectra were 5% and those for ^{13}C NMR spectra, 10%. The GLC analysis was fulfilled on a Shimadzu QP2010 Plus gas chromatography mass spectrometer in the electron impact mode at 70 eV with subsequent scanning in the *m/z* range from 40 to 350 Da; an Equity 5 capillary column (30 m × 0.25 mm, 95% of dimethylpolysiloxane, 5% of diphenylpolysiloxane, carrier gas helium). Optical rotation of samples was determined on an ADP410 automatic digital polarimeter at a wavelength of 589 nm (cell length 50 mm, concentration of solutions 2–30 g/100 mL of methanol). Excess of enantiomers in products was determined on a GC Agient 7890(A) gas chromatograph equipped with a Dean switch, a flame ionization detector, and a CYCLODEX-B chiral capillary column (length 30 m, internal diameter 0.25 mm).

Molecular geometry of rhodium(1+) complexes was optimized using the B3LYP hybrid functional on the Firefly version 8.1 software package [32]. The Lanl2dz basis set was used for rhodium atom and 6-31(G)(d) for other atoms.

***N,N*'-(1*R*,2*R*)-Cyclohexane-1,2-diylbis[1-(pyridine-2-yl)methanimine] (2a).** A solution of 4.4 mmol (0.5 g) of (*R,R*)-1,2-cyclohexanediimine **1** {$[\alpha]_D$ –8.17°C (*c* 8.7, C_6H_6)} in 30 mL of methanol was boiled for 30 min, then a solution of 9 mmol (0.96 *g*) of 2-pyridine-carboxaldehyde in 20 mL of methanol was added dropwise. The mixture was stirred for 4 h and left overnight. The reaction was monitored by the TLC method up to the complete aldehyde conversion. A white precipitate was filtered off, washed with hexane, and dried. Yield 78% (0.91 g) $[\alpha]_D^{23}$ 264 (*c* 1.0, MeOH), mp 126–127°C, (mp 128–129°C [34]). IR spectrum, (KBr), ν, cm^{-1}: 1645 m (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.45–1.52 m (2H, $C^{3,6}\underline{H}_AH_B$), 1.79–1.87 m (2H, $C^{3,6}H_A\underline{H}_B$, 4H $C^{4,5}H_AH_B$), 3.43–3.58 m (2H, $NC^{1,2}H$) 7.18 d.d. (2H, $C^{11,11'}H$, $^3J_{HH}$ = 7.5, 4.8 Hz), 7.60 d.d (2H, $C^{10,10'}H$, ^3J = 7.5, 1.5 Hz), 7.85 br.d (2H, $CH^{9,9'}H$, ^3J = 7.5 Hz), 8.28 s (2H, CH=N), 8.51 d (2H, $C^{12,12'}\underline{H}$). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.50–1.62 m (2H, $C^{3,6}\underline{H}_AH_B$), 1.81–1.91 m (2H, $C^{3,6}H_A\underline{H}_B$; 4H $C^{4,5}H_AH_BH$), 3.49–3.58 m (2H, $NC^{1,2}\underline{H}$), 7.37 d (2H, $C^{11,11'}H$, ^3J = 5.5 Hz), 7.80 d.d (2H, $C^{10,10'}H$, ^3J = 7.8, 1.2 Hz), 7.90 d (2H, $C^{12,12'}H$, *J* = 5.5 Hz). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm: 24.7 ($C^{4,5}$), 32.9 ($C^{3,6}$), 74.0 ($C^{1,2}$), 121.6 ($C^{9,9'}$), 125.5 ($C^{11,11'}$), 137.3 ($C^{10,10'}$), 149.0 ($C^{12,12'}$), 154.7 (N=CH), 161.4 ($C^{8,8'}$). Found, %: C 73.91; H 6.81; N 19.10. $C_{26}H_{24}N_4$. Calculated, %: C 73.97; H 6.85; N 19.18.

***N,N*'-(1*R*,2*R*)-Cyclohexane-1,2-diylbis-[1-(quinoline-2-yl)methanimine] (2b)** was obtained similarly**.** Yield 62% (1.0 g) $[\alpha]_D^{23}$ +41.4 (*c* 1.0, MeOH); $[\alpha]_D^{23}$ +92.0 (*c* 1.0, CH_2Cl_2); $[\alpha]_D^{23}$ + 90.3 (*c* 1.0, CH_2Cl_2) [35]; mp 207–208°C (C_2H_5OH) (mp 205–208 [36], 212–214°C [37]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.50–1.58 m (2H, $C^{3,6}H_AH_B$), 1.82–1.92 m (2H, $C^{3,6}\underline{H}_A\underline{H}_{(B)}$, 4H, $C^{4,5}\underline{H}_A\underline{H}_BH$), 3.61–3.66 m (2H,

N–C^{1,2}H), 7.46 d.d (2H, C$^{10,10'}$H, ^3J = 7.3, 1.0 Hz), 7.63 d.d (2H, (C$^{10,10'}$H, ^3J = 7.6, 1.5 Hz), 7.71 d (2H, C$^{10,10'}$H, ^3J = 8.2 Hz), 8.00 d (2H, C$^{9,9'}$H, ^3J = 8.6 Hz), 8.05 d (2H, C$^{11,11'}$H, ^3J = 3.5 Hz), 8.06 d (2H, C$^{11,11'}$H, ^3J = 3.0 Hz), 8.50 s (2H, CH=N). Found, %: C 79.52; H 6.05; N 14.21. $C_{26}H_{24}N_4$. Calculated, %: C 79.59; H 6.12; N 14.29.

***N,N'*-(1*R*,2*R*)-Cyclohexane-1,2-diylbis[1-(thiene-2-yl)methanimine] (2c).** The compound was obtained similarly**.** Yield 74% (0.7 g), $[\alpha]_D^{23}$ 520 (*c* 1.0, MeOH), mp 135–136°C (mp 137°C [37]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30–1.38 m (2H, C^{3,6}H$_A$H$_B$), 1.60–1.69 m (2H, C^{3,6}H$_A$H$_B$), 1.69–1.78 m (4H, C^{4,5}H$_A$H$_B$), 3.18–3.24 m (2H, N–C^{1,2}H), 6.84 t (2H, C$^{10,10'}$H, ^3J = 4.3 Hz), 7.02 d (2H, C$^{9,9'}$H, ^3J = 4.5 Hz), 7.17 d (2H, C$^{11,11'}$H, ^3J = 4.5 Hz), 8.16 s (2H, CH=N). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm: 24.3 (C^{9,10}), 32.5 (C^{8,11}), 73.3 (C^{6,7}), 127.1 (C$^{3,3'}$), 128.1 (C$^{3,3'}$), 130.0 (C$^{2,2'}$), 142.5 (C$^{2,2'}$), 154.2 (CH=N). Found, %: C 63.46; H 5.88; N 9.20; S 21.10. $C_{16}H_{18}N_2S_2$. Calculated %: C 63.58; H 5.97; N 9.27; S 21.19.

***N,N'*-(1*R*,2*R*)-Bis(pyridine-2-yl-methyl)cyclohexane-1,2-diamine (2d).** The diamine was obtained by reduction of 30 mL of compound **2a** (0.8 g) alcohol solution with sixfold $NaBH_4$ excess at room temperature. After 20 h mixing and removal of the solvent the formed white precipitate was washed several times by diethyl ether, the joint extract was washed with distilled water and dried over Na_2SO_4. After removal of the solvent white precipitate was recrystallized from ethanol. Yield 82%, mp 134.8–136.6°C. ^{1}H NMR spectrum **(**$CDCl_3$), δ, ppm: 1.11–1.21 m (4H, C^{4,5}H$_A$H$_B$), 1.64 d.d (2H, C^{3,6}H$_A$H$_B$, ^3J = 9.2), 2.07 d (2H, C^{3,6}H$_A$H$_B$, ^3J = 12.5), 2.23-2.28 m (2H, NC^{1,2}H), 2.44 br.s (2H, NH), 3.77 d (2H, CH$_A$H$_B$), 3.95 d (2H, C H$_A$H$_B$), 7.06 t (2H, C$^{11,11'}$H, ^3J = 6 Hz), 7.32 d (2H, C$^{9,9'}$H, ^3J = 7.8 Hz), 7.54 d (2H, CH$^{10,10'}$H, ^3J = 7.8 Hz), 8.45 (2H, C$^{12,12'}$H, ^3J = 4.5 Hz). Found, %: C 73.11; H 8.03; N 18.86. $C_{16}H_{24}N_4$. Calculated, %: C 72.97; H 8.11; N 18.92.

Complex 3a. To a solution of 0.1 mmol (0.0493 g) of [Rh(cod)Cl]Cl_2 in THF a solution of 0.2 mmol (52.8 mg) of ligand **2a** in a small THF amount was added. The mixture was stirred for 6 h, then evaporated to a volume of 3 mL. A red-burgundy precipitate was washed several times by diethyl ether and dried in a vacuum at 30–40°C. ^{1}H NMR spectrum (*i*-PrOH), δ, ppm: 1.60–1.72 m, (2H, C^{4,5}H$_A$H$_B$), 1.84–1.96 m (2H, C^{3,6}H$_A$H$_B$; 4H C^{4,5}H$_A$H$_B$), 1.96–2.09 m (4H, cod-CH$_A$H$_B$), 2.24–2.48 (4H, cod-CH$_A$H$_B$), 3.23–3.39 m (2H, NC^{1,2}H), 4.30–4.42 (1H, cod-CH$_{vinyl}$), 4.66–4.76 m (1H, cod-CH$_{vinyl}$), 4.75–4.85 m (2H, cod-CH$_{vinyl}$), 7.50 t (1H, C^{10}H, ^3J = 6.0 Hz), 7.80 t (1H, C$^{10'}$H, ^3J = 6.0 Hz), 7.96 t (2H, C$^{9,9'}$H, ^3J = 7.5 Hz), 8.19 d (2H, C^{8}H, C$^{2'}$H, ^3J = 7.5 Hz), 8.34 d (1H, C^{11}H, ^3J = 7.5 Hz), 8.38–8.42 m (1H, CH=N), 8.56 d (1H, C$^{11'}$H, ^3J = 4.5 Hz), 9.36–9.45 m (1H, C'H=N). ^{13}C NMR spectrum (*i*-PrOH), δ_C, ppm: 28.7 (cod-CH$_2$), 30.7 (cod-CH$_2$), 32.6 (C^3), 34.2 (C^{4,5}), 35.7 (C^6), 53.1 (C^2); 66.5 (C^1), 73.8 (cod-CH$_{vinyl}$), 81.0 (cod-CH$_{vinyl}$), 121.6 (C^{11}); 126.1 (C$^{11'}$); 129.5 (C^9), 130.4 (C$^{9'}$), 137.6 (C^{10}), 141.7 (C$^{10'}$), 149.6 (C^{12}); 150.6 (C^8), 154.5 (N=CH); 155.9 (C$^{12'}$), 162.1 (C$^{8'}$); 173.1 (N=C'H).

Transfer hydrogenation of acetophenone. The cyclooctadiene dimeric complex [Rh(1,5-COD)μ-Cl]$_2$ (0.025 mmol, 12.4 mg) and 25 mL of 2-propanol were placed in a vessel with a jacket of 100 mL blown through with dry argon. To the bright yellow solution of the complex 0.05 mmol of the ligand was added and the reaction mixture was stirred for 15 min. As this took place, the solution changed from pale yellow to red-brown. Then 0.05 mol KOH or *t*-BuOK in 20 mL of 2-propanol were added and the mixture was stirred for 15 min. To the resulting bluish-green solution 0.2 mL of hexadecane as an internal reference and 0.5 mL (4.3 mmol) of acetophenone were added. Then the temperature was quickly raised to 78°C, and the reaction course was traced by the GLC-MS method by sampling at 5–10 min intervals. The analysis was performed on a GC-MS Shimadzu QP2010 Plus chromatomass-spectrometry system and a GC Agient 7890A gas chromatograph. Configuration of the prevailing product was determined by com-parison with the published data [38].

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