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New C_2-Symmetric Optically Active Salen Ligands and Their Cobalt(II) Complexes. Hydridoborate Reduction of Prochiral C=O and C=C Bonds

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Abstract—Novel optically active salen ligands and their cobalt(II) complexes were synthesized on the basis of 1,3-dioxolane. Spectral parameters of the complexes and their catalytic activity in enantioselective reduction of carbonyl and unsaturated compounds with sodium tetrahydridoborate were studied. The catalytic reduction of acetophenone is characterized by quantitative yield, the optical yields ranging from 0 to 42%. Benzil and ethyl benzoylformate undergo noncatalytic reduction. The catalytic activity and enantioselectivity in the reduction prochiral C=C bond strongly depend on the solvent and change from low to moderate values in the reduction of methyl 2-acetylamino-3-phenylprop-2-enoate. Dimethyl 2-methylidenebutane-1,4-dioate is reduced in DMF and its mixtures with ethanol and toluene in quantitative yield; in chloroform, the optical yield reaches 89%, but the chemical yield sharply decreases.

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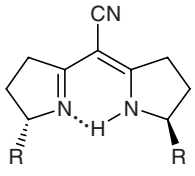
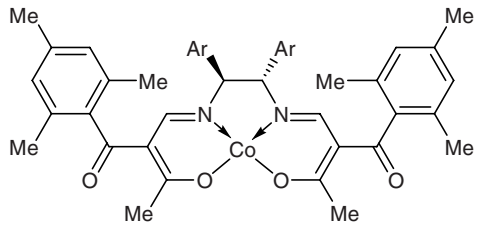
Metal complexes with optically active Schiff base ligands have been introduced into synthetic practice as enantioselective catalysis relatively recently, about 15 years ago. The first representatives of these compounds were metal complexes with chiral C_2-symmetric chelating semicorrin ligands **I** which were prepared from D- or L-pyroglutamic acid [1]; these catalyst were shown to be effective in enantioselective catalytic hydrogenation of prochiral C=C bonds, e.g., in unsaturated carboxylic acids, their esters and amides [2, 3], nitriles, sulfones, and phosphonates [4]. Schiff bases and aromatic and heteroaromatic ketones were reduced with sodium tetrahydridoborate in the presence of chiral β-oxo aldehyde imine cobalt(II) complexes **II** with optical yields of up to 92% [5–7]; the reduction with $NaBH_4$ modified by alcohols ensured up to 97% enantiomeric excess, the conversion being quantitative [8–10].



I

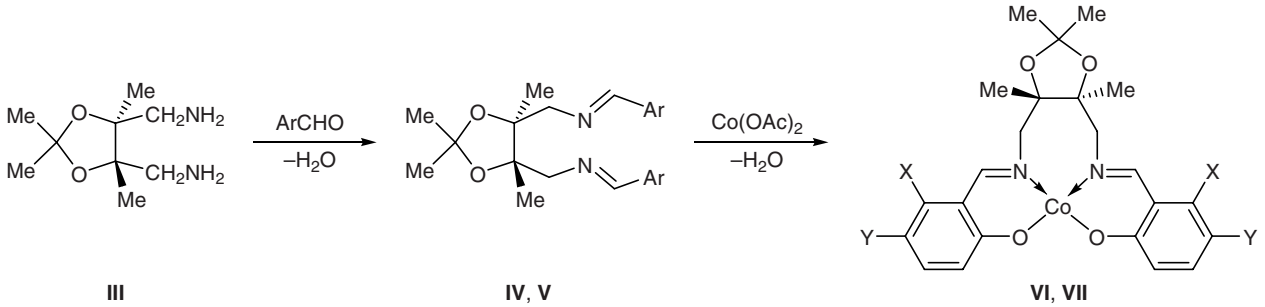


II

R = *t*-$BuPh_2SiOCH_2$ (**a**), $EtOCH_2$ (**b**), $HOC(Me)_2$ (**c**);
Ar = Ph (**a**), 3,5-$Me_2C_6H_3$ (**b**), 2,4,6-$Me_3C_6H_2$ (**c**).

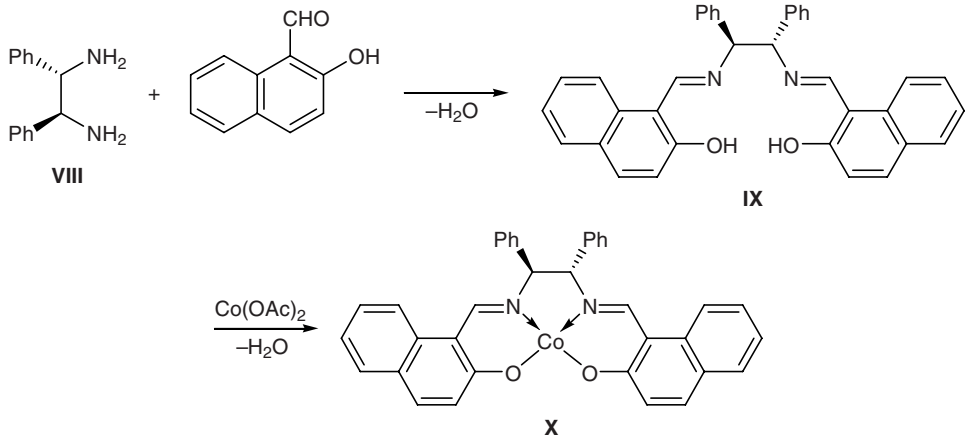
A specific place among chiral imine ligands is occupied by Schiff bases formed by reaction of C_2-symmetric diamines with salicylaldehyde or structurally similar aromatic aldehydes having a hydroxy group in the *ortho* position with respect to the aldehyde group. These ligands (generically named *salen*) are structurally related to the ligands in complexes **II**; they have four coordination centers (two oxygen and two nitrogen atoms) and are capable of forming complexes with many metals. Their complexes exhibit a high catalytic activity and enantioselectivity in various processes, including epoxidation, aziridination, cyclopropanation, opening of oxirane and aziridine rings, Diels–Alder

Scheme 1.



III **IV**, **V** **VI**, **VII**

IV, Ar = 2-HOC_6H_4; **V**, Ar = 2-$HOC_{10}H_6$; **VI**, X = Y = H; **VII**, XY = CH=CH–CH=CH.



VIII **IX** **X**

cyclizations and heterocyclizations, hydridoborate reduction, conjugate addition, etc. [11–26]. Such catalysts were called *privileged* due to seeming contradiction between their high enantioselectivities in various reactions (i.e., low selectivity for the type of process) [25, 26].

Almost all known chiral salen ligands and their complexes with metals were synthesized from optically active 1,2-diarylethane-1,2-diamines or cyclohexane-1,2-diamines. As far as we know, the only exceptions are chiral salen metal complexes based on binaphthyldiamine, which were used in the synthesis of cyclic carbonates [27]. As a rule, these metal complexes had a C_2 symmetry, i.e., the initial Schiff bases were obtained by reaction of diamine with 2 equiv of salicylaldehyde or its substituted derivatives. Nevertheless, some unsymmetrical chiral salen ligands were also reported; they were prepared by stepwise condensation of a diamine, e.g., with unsubstituted and substituted salicylaldehydes [28].

In the present article we report on the synthesis of novel salen ligands **IV** and **V** based on (4*S*,5*S*)-4,5-bis(aminomethyl)-2,2-dimethyl-1,3-dioxolane (**III**) and their cobalt(II) complexes **VI** and **VII**. The IR and UV spectra of the new ligands and complexes derived therefrom were studied. We also synthesized a salen ligand from (1*R*,2*R*)-(+)-1,2-diphenylethene-1,2-diamine (**VIII**) and 2-hydroxynaphthalene-1-carbdehyde and the corresponding complex with cobalt. The catalytic activity of the obtained metal complexes was estimated in the reduction of acetophenone, benzil, and ethyl benzoylformate with sodium tetrahydridoborate.

Diamine **III** was prepared by an improved procedure [29]. Compounds **III** and **VIII** smoothly reacted with aromatic aldehydes to give Schiff bases **IV**, **V**, and **IX**, which were treated with cobalt(II) acetate to

Table 1. IR spectra (cm^{-1}) of salen ligands **IV**, **V**, and **IX** and complexes **VI**, **VII**, and **X**

Comp. no.	ν(C=N)	ν(C–O)	ν(Co–N)	ν(Co–O)	ν(O–H)
IV	1632 s	1278 s	–	–	2660–2740
V	1630	1260 m	–	–	2620–2730
VI	1613 s	1317 s	465 s	425 s	–
VII	1616 s	1283 m	475 s	418 s	–
IX	1624 s	1266 m	–	–	2720–2750
X	1616 s	1311 w	475 s	420 s	–

obtain complexes **VI**, **VII**, and **X** (Scheme 1). The structure of ligands **IV**, **V**, and **IX** was confirmed by the IR and NMR spectra and elemental analyses.

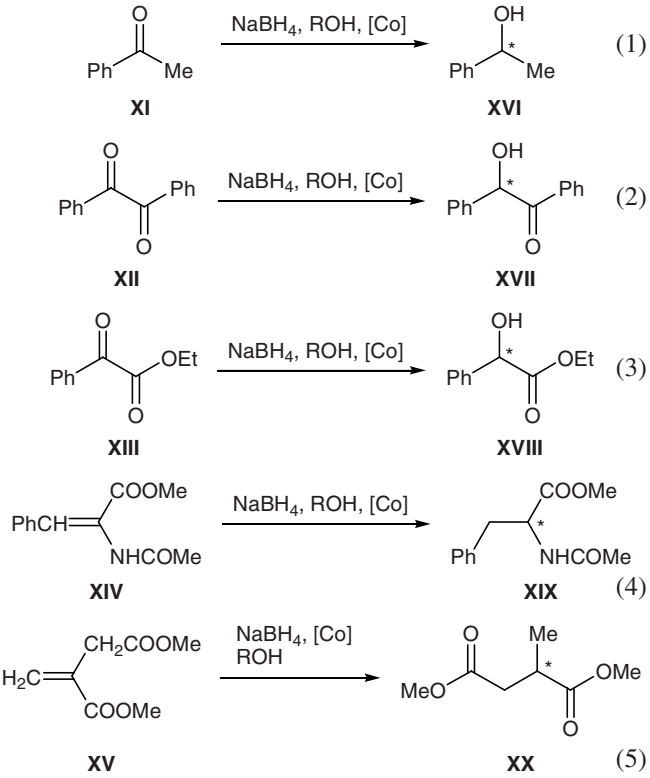
We examined the effect of metal coordination at donor sites of the ligand on the vibrational (Table 1) and electronic spectra of compounds **IV**–**VII**, **IX**, and **X**. The IR spectra of the free ligands contain broad bands in the region 2600–2750 cm^{-1} which belong to stretching vibrations of the OH groups involved in intermolecular hydrogen bonds OH···N. No such bands are present in the spectra of the complexes. Stretching vibrations of the C=N group in the free ligands appear at 1624–1632 cm^{-1}; complex formation leads to displacement of the C=N band to lower frequencies due to coordination of the nitrogen atom to the metal ion. The above differences are most clearly seen in the IR spectra of ligand **IV** and its complex **VI**. The spectral patterns of the other ligand–complex couples in that region are complicated due to absorption of the naphthalene ring. Analogous low-frequency shift (up to 20 cm^{-1}) was observed in the IR spectra of structurally related copper(II) complexes with Schiff bases [30]. The ν(C–O) band in the spectra of the complexes is strongly displaced toward higher frequencies owing to increase in the order of the C–O bond upon substitution of hydrogen by cobalt ion. Coordination to metal also gives rise to new bands in the regions 465–475 and 418–425 cm^{-1}, which are typical of ν(Co–N) and ν(Co–O) vibrations in cobalt(II) complexes.

The electronic absorption spectrum of complex **VI** is characterized by increased intensity of the band at λ 255 nm. The latter originates from π→π* electron transition in the phenol chromophore. A strong red shift is observed only for the long-wave absorption maximum of ligand **IV** (λ 318 nm) upon coordination to cobalt (λ 384 nm for complex **VI**). The maximum at λ 384 nm in the spectrum of **VI** arises from mixed electron transitions: charge transfer from p_π orbitals of the donor centers in the ligand to *d* orbitals of the transition metal and *n*→π* transition from the C=N group to the phenyl ring. The intensity of the long-wave absorption band decreases in going from ligand **IV** to complex **VI**. Likewise, the electronic absorption spectra of complexes **VII** and **X** are characterized by reduced intensity of the doublet long-wave band (λ_{max} 400/420 nm) as compared to the free ligands, the position of that band remaining unchanged.

The new complexes are more advantageous than the diamine Co(II) chloride complexes studied previously for the following reasons: (1) the nitrogen atoms in the Schiff bases are sp^2-hybridized and are therefore less basic than sp^3-hybridized nitrogen atoms in diamines; as a result, reduction of the central metal ion to zero-valence state with the ligand becomes less probable; (2) four-dentate ligand ensures more complete flanking of the metal ion, giving rise to a rigid chelate structure with restricted mobility of the ligand.

In continuation of our previous studies on enantioselective borohydride reduction in the presence of cobalt complexes [31], the obtained salen complexes were tested as catalysts in the reduction of the C=O group in acetophenone (**XI**), benzil (**XII**), and ethyl benzoylformate (**XIII**) and of the C=C bond in methyl 2-acetylamino-3-phenylprop-2-enoate (**XIV**) and dimethyl 2-methylidenebutanedioate (**XV**) with sodium tetrahydridoborate (including the reagent modified with alcohols) (Scheme 2).

Scheme 2.



We found that the catalytic activity and enantioselectivity in the reduction of carbonyl compounds **XI**–**XIII** strongly depend on the solvent. As the latter we tried chloroform, diethylene glycol dimethyl ether (diglyme), and DMF. The catalytic reduction of acetophenone with $NaBH_4$ in the presence of complex **VI** in THF [reaction (1)] gave 66% of 1-phenylethanol; in DMF, diglyme, and ethanol the yield of **XVI** was

Table 2. Yields of 1-phenylethanol (**XVI**) and enantioselectivities (enantiomeric excess, ee) in the reduction of acetophenone (**XI**) with $NaBH_4$ in the presence of complex **VI** (c_{cat} = 8–10 mM, reaction time 5–7 h)

Run no.	Ratio **VI**:**XI**:$NaBH_4$:(EtOH)	Solvent	Temperature, °C	Yield, %	ee, % (enantiomer)
1	1:80:40	THF	20	66	1.2 (*R*)
2	1:80:40	EtOH	–20	100	1.4 (*R*)
3	1:80:40	DMF	–15	100	1.6 (*R*)
4	1:80:50	Diglyme	–15	100	1.1 (*R*)
5	1:80:50	THF	–15	100	1.4 (*R*)
6	1:70:40:(80)	$CHCl_3$	–20	8.4	2.1 (*S*)
7	1:70:40:(80)[a]	$CHCl_3$	–20	19.4	0.6 (*S*)
8	1:100:150:(300)	$CHCl_3$	–20	100	0.4 (*S*)

[a] With addition of 1 mol of PPh_3 per mole of complex **VI**.

Table 3. Yields of 1-phenylethanol (**XVI**) and enantioselectivities in the reduction of acetophenone (**XI**) with $NaH_2B(OEt)_2$ in chloroform (c_{cat} = 1.6 mM, 22°C) in the presence of complexes **VI**, **VII**, and **X**

Complex no.	Reaction time, h	Yield, %	ee, % (enantiomer)	TOF,[a] h^{-1}
No catalyst	72	7.5	–	
VI	26	61	8.5 (*R*)	3.5
VII	24	75	10.5 (*R*)	4.7
X	23	63.5	42.3 (*R*)	4.1

[a] TOF stands for turnover frequency.

quantitative, but in all cases the enantioselectivity was poor, and we failed to raise it by varying the temperature, solvent nature, or composition of the catalytic system (Table 2). In the presence of a large excess of ethanol, the reduction was quantitative even at low temperature (Table 2, run no. 8), presumably due to contribution of the noncatalytic process.

Sodium tetrahydridoborate was modified with alcohols to diminish its reducing power and estimate the effect of the alcohol nature on the enantioselectivity.

$$NaBH_4 + 2ROH \longrightarrow NaBH_2(OR)_2 + 2H_2 \quad (6)$$

Raising the temperature from –20°C to ambient and 5–6-fold reduction of the catalyst concentration led to increased enantioselectivity in the reduction of acetophenone with $NaBH_2(OEt)_2$ in chloroform in the presence of complexes **VI**, **VII**, and **X**, the chemical yields remaining sufficiently good (Table 3). The maximal turnover frequency of the catalyst based on complex **X** was attained at the initial part of the kinetic curve and was 20 h^{-1}; this value is several times greater than those reported in the literature [22, 23] at a comparable enantioselectivity. More active substrates than acetophenone, namely benzil (**XII**) and ethyl benzoylformate (**XIII**), underwent noncatalytic reduction with the complex hydride $NaBH_2(OEt)_2$ under the above conditions. We plan to optimize the reduction conditions, for higher enantiomeric excess relative to acetophenone might be expected for ketones containing other functional groups.

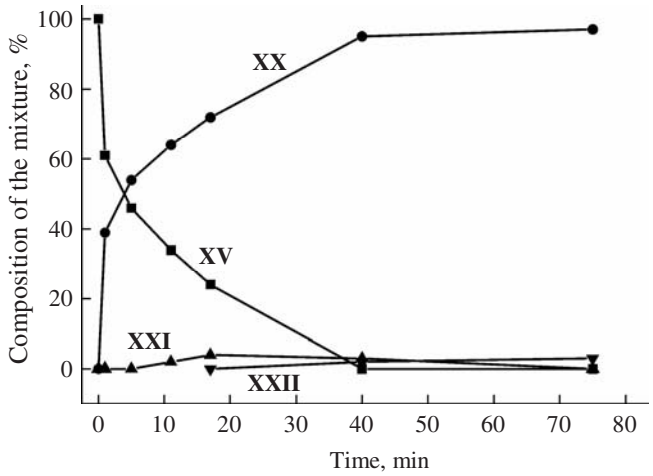
The efficiency of salen cobalt(II) complexes in enantioselective hydrogenation of prochiral unsaturated esters was studied using complex **VI** as an example. Both catalytic activity and enantioselectivity in the hydrogenation of the prochiral C=C bonds in esters **XIV** and **XV** turned out to be quite sensitive to the solvent and modifying alcohol. The enantioselectivity changed up to inversion of the sign of asymmetric induction, from ee 26% (*S*) to 89% (*R*) (Table 4, run nos. 5, 12). According to the GLC data, the reduction of dimethyl 2-methylidenebutanedioate in EtOH–DMF gives dimethyl 2-methylbutanedioate and only traces of the corresponding diethyl ether. However, when the reaction mixture was left to stand overnight (before decomposition), the concentration of diethyl 2-methylbutanedioate increased to 93–96% (Table 4, run nos. 5, 6). Obviously, the reduction is accompanied by transesterification of product **XX**, catalyzed by complex **VI** as Lewis acid.

Table 4. Hydrogenation of unsaturated esters **XIV** and **XV** with $NaBH_4$ in the presence of complex **VI**

Run no.	Substrate no.	Ratio substrate–**VI**–$NaBH_4$ (modifying alcohol)[a]	Solvent	c_{cat}, mM	Reaction time, h	Yield, %	ee, % (isomer)
1	**XIV**	10:1:20	EtOH	10	5	6.0	61.8 (*R*)
2		10:1:20	EtOH–DMF (3:2)	6.7	5	0	–
3		50:1:100 (*i*-PrOH)	DMF–toluene (17:3)	1.0	26	16.7	36.9 (*S*)
4		50:1:100 (MeOH)	DMF–toluene (17:3)	1.0	48	44.8	6.5 (*S*)
5	**XV**	10:1:13	EtOH–DMF (3:2)	12.5	5	100[b]	26.0 (*S*)
6		25:1:20	EtOH–DMF (3:2)	8.0	5	100[c]	12.9 (*S*)
7		63:1:128 (*i*-PrOH + MeOH)	DMF	2.5	5	100	9.0 (*S*)
8		63:1:100 (*i*-PrOH)	DMF–toluene (17:3)	1.0	1	100	7.1 (*S*)
9		63:1:100 (EtOH)	DMF–toluene (17:3)	1.0	1	100	6.5 (*S*)
10		316:1:600 (*i*-PrOH)	DMF–toluene (17:3)	1.0	0.66	100	6.2 (*S*)
11		200:1:400 (*i*-PrOH+MeOH)	DMF–toluene (17:3)	1.0	1	100	7.0 (*S*)
12		20:1:40 (EtOH)	$CHCl_3$	4.0	14	6.0	88.7 (*R*)
13		20:1:40 (EtOH)	$CHCl_3$	4.0	48	11.4	65.9 (*R*)
14		20:1:100 (*i*-PrOH)	$CHCl_3$	1.0	48	7.2	62.0 (*R*)
15		20:1:40	$CHCl_3$	4.0	48	0	–

[a] Amount of alcohol 2 mol (or 1 mol of each alcohol) per mole of $NaBH_4$.
[b] 96% of diethyl 2-methylbutanedioate and 4% of dimethyl 2-methylbutanedioate.
[c] 93% of diethyl 2-methylbutanedioate and 7% of dimethyl 2-methylbutanedioate.

Unlike ester **XV**, coordination of ester **XIV** to the metal complex catalyst is sterically hindered because of the presence of a phenyl group at the double bond. Therefore, ester **XIV** almost does not undergo hydrogenation with sodium tetrahydridoborate in ethanol and ethanol–DMF mixture (Table 4, run nos. 1, 2). By contrast, the hydrogenation of ester **XV** occurs with quantitative chemical yield at substrate-to-catalyst ratios of (10–25):1 in DMF–EtOH; here, enantiomeric excess is 26% with respect to (*S*)-**XX** (Table 4, run nos. 5, 6). The ee value reaches 37% (*S*) in the reduction of ester **XIV** with $NaBH_4$ modified with 2 equiv of isopropyl alcohol. The average reaction rate is lower at least by an order of magnitude that the rate of hydrogenation of **XV** (Table 4; cf. run nos. 3 and 8, 10).



Kinetics plots for the reduction of dimethyl 2-methylidenebutanedioate (**XV**) with $NaH_2B(OPr\text{-}i)_2$ in the presence of complex **VI** (DMF–toluene, 17:3).

An important factor is the solubility of the reducing agent; both sodium tetrahydridoborate and its alcohol-modified derivatives are readily soluble in DMF. In all cases, dimethylformamide-containing systems are yellow–brown and visually homogeneous. No reduction of ester **XV** was observed in pure chloroform (Table 4, run no. 15) because of limited solubility of $NaBH_4$. After modification of $NaBH_4$ with ethanol, substrate **XV** was hydrogenated in a poor chemical yield (1–2 mol per mole of the complex), but the optical yield of the (*R*)-enantiomer of **XX** reached 89%. Thus, variation of the solvent nature leads to inversion of asymmetric induction. These results indicate that the reduction of ester **XV** in chloroform should be carried out using modified sodium tetrahydridoborate (to increase its solubility) and that the modifying alcohol should favor improved stereoselectivity.

As follows from the data in Table 4, the enantioselectivity in the hydrogenation of ester **XV** in DMF is

poor, and it weakly depends on the nature of modifying alcohol. No effect was observed after addition of toluene to DMF (Table 4; cf. run nos. 7 and 8–11). The use of DMF–ethanol as solvent and increase of the catalyst concentration lead to improved enantioselectivity (Table 4; run nos. 5, 6).

We examined the kinetics of the reduction of ester **XV** in DMF–toluene with sodium tetrahydridoborate modified by isopropyl alcohol; the substrate and product concentrations were determined by GLC analysis of samples withdrawn from the reaction mixture (see figure). It was found that the hydrogenation process is accompanied by transesterification of both unsaturated substrate **XV** and its reduction product **XX**. The kinetic data also suggest that diisopropyl 2-methylidenebutanedioate (**XXI**) appears in the reaction mixture after accumulation of a considerable amount of compound **XX** and that diisopropyl 2-methylbutanedioate (**XXII**) is formed in parallel. This means that the transesterification of **XV** and **XX** occurs at a much lower rate than the reduction of **XV**. After 1.5 h, the hydrogenation products were isolated to determine their optical purity. The initial turnover frequency was 7440 h^{-1} ($c_{cat.}$ = 1 M, substrate-to-catalyst ratio 316).

Thus higher optical yields could be attained using chloroform as solvent. The catalytic activity of the complexes in chloroform will be the subject of our further studies.

EXPERIMENTAL

The UV spectra were recorded on a Perkin–Elmer Lambda 35 UV/Vis spectrophotometer from solutions in ethanol. The IR spectra were measured in mineral oil or KBr on a Bruker IFS-25 spectrometer. The ^1H and ^{13}C NMR spectra were obtained on a Bruker DPX 400 instrument (400 MHz for ^1H) from solutions in $CDCl_3$; the chemical shifts were measured relative to tetramethylsilane.

The solvents (acetone, hexane, diethyl ether, methanol, ethanol, propan-2-ol, methylene dichloride, chloroform, and DMF) were purified and dehydrated according to standard procedures. All operations were carried out under argon. Acetophenone and ethyl benzoylformate were purified by vacuum distillation, and benzil was recrystallized from ethanol.

(4*S*,5*S*)-*N*,*N*′-4,5-Bis(salicylidene)(2,2-dimethyl-1,3-dioxolane-4,5-diyl)dimethanamine (IV). A solution of 5.63 g (46.1 mmol) of salicylaldehyde in 150 ml of ethanol was added dropwise over a period of 30–40 min to a solution of 3.69 g (23.1 mmol) of (4*S*,5*S*)-(2,2-dimethyl-1,3-dioxolane-4,5-diyl)dimethanamine (**III**) in 150 ml of ethanol, heated at the boiling point. The mixture was stirred for 2 h and left overnight, and the precipitate (pale yellow needles) was filtered off, washed with ethanol, and dried. Yield 5.1 g (60%), mp 109–110°C, $[\alpha]_{546}$ = –59.8±1.1° (*c* = 0.88, EtOH). UV spectrum, λ, nm (logε): 215 (4.62), 222 (4.57), 256 (4.36), 318 (3.88). IR spectrum, ν, cm^{-1}: 2985, 2881, 1629, 1585, 1490, 1450, 1420, 1360, 1265. ^1H NMR spectrum, δ, ppm: 1.37 s (6H, CH_3), 3.84 m (4H, CH_2), 4.21 m (2H, OCH), 6.86 t (2H, 5-H, *J* = 7.4 Hz), 6.95 d (2H, 3-H, *J* = 8.3 Hz), 7.23 d (2H, 6-H, *J* = 7.6 Hz), 7.30 t (2H, 4-H, *J* = 7.6 Hz), 8.36 s (2H, CH=N), 13.06 s (2H, OH). ^{13}C NMR spectrum, δ_C, ppm: 27.21 (CH_3), 60.97 (CH_2), 77.94 (OCH), 109.45 (**C**Me_2), 117.08 (C^3), 118.71 (C^1), 118.78 (C^5), 131.65 (C^6), 132.61 (C^4), 161.05 (C^2), 167.50 (C=N). Found, %: C 67.90; H 6.56; N 7.72. $C_{21}H_{24}N_2O_4$. Calculated, %: C 68.46; H 6.57; N 7.60.

(4*S*,5*S*)-*N*,*N*′-4,5-Bis(2-hydroxynaphthalen-1-ylmethylidene)(2,2-dimethyl-1,3-dioxolane-4,5-diyl)dimethanamine (V). A solution of 0.5 g (2.9 mmol) of diamine **III** in 30 ml of methanol was heated to the boiling point, a solution of 1 g (5.8 mmol) of 2-hydroxynaphthalene-1-carbaldehyde in 20 ml of methanol was added over a period of 30–40 min, and the mixture was stirred for 2 h and left overnight. The large yellow crystals were filtered off, washed with hexane, and dried. Yield 0.99 g (73%), mp 192–193°C, $[\alpha]_{546}$ = –170.5° (*c* = 1.07, $CHCl_3$). UV spectrum, λ, nm (logε): 292 (4.92), 251 (4.57), 261 (4.42), 267 (4.16), 305 (4.29), 318 (3.88), 333 (4.01), 380 (4.06), 401 (4.30), 419 (4.33). IR spectrum, ν, cm^{-1}: 2910, 2890, 2620–2730, 1610. ^1H NMR spectrum, δ, ppm: 1.39 s (6H, CH_3), 3.91 m (4H, CH_2), 4.21 m (2H, OCH), 6.97 d (2H, 3-H), 7.26 t (2H, 6-H), 7.39 t (2H, 7-H), 7.63 d (2H, 5-H), 7.71 d (2H, 4-H), 7.87 d (2H, 8-H), 8.91 s (2H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 27.13 (CH_3), 55.95 (CH_2), 77.35 (OCH), 107.55 (CMe_2), 110.03 (C^1), 118.45 (C^9), 123.15 (C^7), 123.24 (C^3), 126.81 (C^5), 128.04 (C^8), 129.25 (C^6), 133.38 (C^{10}), 136.79 (C^4), 160.91 (C^2), 172.48 (C=N). Found, %: C 74.58; H 6.34; N 6.31. $C_{29}H_{28}N_2O_4$. Calculated, %: C 74.34; H 6.02; N 5.98.

(1*R*,2*R*)-1,2-Diphenyl-*N*,*N*′-bis[(*E*)-2-hydroxynaphthalen-1-ylmethylidene]ethane-1,2-diamine (IX) was synthesized in a similar way. Yield 84%, mp 245–247°C, $[\alpha]_{546}$ = –13.0° (*c* = 1.0, $CHCl_3$). UV spectrum, λ, nm (logε): 232 (4.87), 251 (4.5), 271

(3.99), 305 (4.44), 313 (4.2), 338 (4), 365 (3.89), 402 (4.08), 425 (4.06). IR spectrum, ν, cm^{-1}: 2720–2750, 1624, 1266. ^1H NMR spectrum, δ, ppm: 4.90 s (2H, CHN), 7.00 d (2H, 3-H), 7.24 m (12H, 3-H, C_6H_5), 7.35 t (2H, 7-H), 7.56 d (2H, 5-H), 7.61 d (2H, 4-H), 7.80 d (2H, 8-H), 8.96 s (2H, CH=N), 15.28 s (2H, OH). ^{13}C NMR spectrum, δ_C, ppm: 78.10 (CHN), 108.11 (C^1), 118.89 (C^8), 121.52 (C^3), 123.12 (C^6), 127.14 (C^{4a}), 127.73 (C^o, C^p), 128.07 (C^7), 128.75 (C^m), 129.03 (C^5), 132.94 (C^i), 135.67 (C^4), 138.70 (C^{8a}), 161.32 (C^2), 168.11 (C=N).

Complex VI was synthesized according to the procedure reported in [32]. Ligand **IV**, 0.4 g (1.1 mmol), was added to a solution of 0.25 g (1 mmol) of cobalt(II) acetate in 20 ml of methanol, the mixture was heated with stirring for 1.5 h under reflux, the solvent was distilled off, and the residue was dried under reduced pressure at 60°C. Yield 0.34 g (80%), mp >330°C (from methanol), $[\alpha]_{546} = -372.3°$ (c = 0.18, EtOH). UV spectrum, λ, nm (logε): 225 (4.47), 255 (4.51), 384 (3.68). IR spectrum, ν, cm^{-1}: 1613, 1317, 465, 425. Found, %: C 57.58; H 4.64; N 6.81. Calculated, %: C 57.44; H 4.57; N 7.05.

Complexes **VII** and **X** were synthesized in a similar way.

Complex VII. Yield 71%, mp >330°C, $[\alpha]_{546} = -293.8°$ (c = 0.097, EtOH). UV spectrum, λ, nm (logε): 231 (4.73), 251 (4.4), 260 (4.28), 269 (1.29), 401 (4.11), 306 (4.13), 333 (3.89), 380 (3.88), 419 (4.06). IR spectrum, ν, cm^{-1}: 1616, 1283, 475, 418. Found, %: C 65.58; H 4.64; N 5.21. Calculated, %: C 65.2; H 4.46; N 5.63.

Complex (X). Yield 68%, $[\alpha]_{546} = +540°$ (c = 0.01, $CHCl_3$). UV spectrum, λ, nm (logε): 264 (4.86), 318 (4.53), 365 (4.2), 404 (4.23), 424 (4.18). IR spectrum, ν, cm^{-1}: 1616, 1311, 475, 420. Found, %: C 75.01; H 4.64; N 4.81. Calculated, %: C 74.67; H 4.54; N 4.85.

Reduction of compounds XI–XV (*general procedure***).** Sodium tetrahydridoborate was modified by adding 2 equiv of methanol, ethanol, or propan-2-ol to a suspension of 77 mg (2 mmol) of $NaBH_4$ in 15 ml of chloroform or DMF under stirring. To the solution thus obtained we added a solution of 8.5 mg (0.02 mmol) of salen cobalt(II) complex in a mixture of 2 ml of chloroform or DMF and 3 ml of toluene, 1–2.5 mmol of substrate **XI–XV** was then added (before addition of acetophenone, the mixture was cooled to –20 to 0°C), and the mixture was stirred for several hours to 2 days. The reaction was terminated by adding 1–2 ml of a saturated solution of ammonium chloride, the mixture was extracted with an organic solvent (methylene chloride, chloroform, or diethyl ether), the extract was washed with water and dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was distilled or (in the reduction of **XIV** and **XV**) purified by column chromatography on silica gel using hexane–ethyl acetate as eluent. The conversion of acetophenone, ethyl benzoylformate, and dimethyl 2-methylidenebutanedioate (**XV**) was determined by GLC using a calibration curve, the conversion of ester **XIV** was determined by ^1H NMR spectroscopy from the intensity ratio of the acetyl proton signals of compounds **XIV** (δ 2.14 ppm) and **XIX** (δ 1.96 ppm), and the conversion of benzil was determined by ^1H NMR spectroscopy from the intensity of the CH(OH) signal.

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