Russian Chemical Bulletin, International Edition, Vol. 54, No. 2, pp. 348—353, February, 2005

Borohydride reduction of acetophenone and esters of dehydrocarboxylic acids in the presence of chiral cobalt(II) diamine complexes

L. O. Nindakova* and B. A. Shainyan

A. E. Favorskii Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,
2 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: +7 (395 2) 39 6046. E-mail: bagrat@irioch.irk.ru

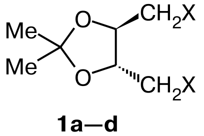
The catalytic reduction of acetophenone, methyl α-acetamidocinnamate, and dimethyl itaconate with alcohol-modified sodium borohydride was studied in the presence of complexes $CoCl_2 \cdot L_2$ (L_2 are chiral C_2-symmetric diamines: (4*S*,5*S*)-2,2-dimethyl-4,5-bis(aminomethyl)-1,3-dioxolane, (4*S*,5*S*)-2,2-dimethyl-4,5-bis(methylaminomethyl)-1,3-dioxolane, (4*S*,5*S*)-2,2-dimethyl-4,5-bis(dimethylaminomethyl)-1,3-dioxolane, and (4*S*,5*S*)-2,2-dimethyl-4,5-bis(diphenylaminomethyl)-1,3-dioxolane). The maximum enantiomeric excess of (*S*)-1-phenylethanol was 24%, that of dimethyl α-methylsuccinate was 38%.

Key words: borohydride reduction, cobalt(II) complexes, chiral diamines.

Alcohol solutions of $NaBH_4$ are known to react with Co^{II} salts to give cobalt metal, $Co(BH_4)_2$, or complex cobalt hydrides, depending on the reaction conditions.[1] It is assumed that the selective reduction of alkenes and alkynes involves cobalt hydrides. For example, aqueous solutions of sodium borohydride containing catalytic amounts of $Co(CN)_5{}^{3-}$ readily reduce α,β-unsaturated acids in a nitrogen atmosphere with participation of $HCo(CN)_5{}^{3-}$, which is rapidly formed in this system;[2] $Co(bpy)_3{}^{+}$, resulting from the reaction of $Co(bpy)_3{}^{2+}$ with $NaBH_4$, efficiently reduces substrates through electron transfer followed by the protonation of the primary products.[3] Cyanamino cobalt systems with tertiary di- and polyamines are known to catalyze hydrogenation of activated olefins with molecular hydrogen in aqueous ethanol under mild conditions.[4]

Asymmetric hydrogenation of prochiral unsaturated compounds with sodium borohydride catalyzed by cobalt complexes with bidentate *N*,*N*-ligands is represented by reduction of esters and amides of unsaturated carboxylic acids in the presence of semicorrin Co^{II} complexes[5—7] and reduction of aromatic ketones, imines, and α,β-unsaturated carboxylates in the presence of Co^{II} oxoaldiminate complexes.[8—11]

This study deals with the influence of a number of chiral C_2-symmetric diamines containing a dioxolane ring, which imparts rigidity to the chiral base of the ligand, namely, (4*S*,5*S*)-2,2-dimethyl-4,5-bis(aminomethyl)-1,3-dioxolane (**1a**), (4*S*,5*S*)-2,2-dimethyl-4,5-bis(methylaminomethyl)-1,3-dioxolane (**1b**), (4*S*,5*S*)-2,2-dimethyl-4,5-bis(dimethylaminomethyl)-1,3-dioxolane (**1c**), and (4*S*,5*S*)-2,2-dimethyl-4,5-bis(diphenylaminomethyl)-1,3-dioxolane (**1d**), on the catalytic reduction of acetophenone (**2**), methyl α-acetamidocinnamate (**3**), and dimethyl itaconate (**4**) with sodium borohydride in the presence of cobalt(II) complexes with these ligands.



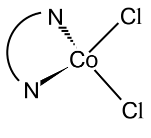
1a—d

X = NH_2 (**a**), NHMe (**b**), NMe_2 (**c**), NPh_2 (**d**)

Results and Discussion

Optically active ligands **1a—d** obtained from tartaric acid[12,13] have been studied in our previous works in enantioselective hydrogenation of dehydroamino acids with molecular hydrogen[12] and reduction of acetophenone through the transfer of hydrogen from the Pr^iOH—KOH system on chiral Rh^I triflate diamine complexes, $[Rh(\mathbf{1a})_2]^+TfO^-$ and $[Rh(COD)(\mathbf{1b})]^+TfO^-$ (COD is cyclooctadiene).[14]

The reaction of equimolar amounts of anhydrous $CoCl_2$ and diamines **1a—c** gave individual diamine complexes $CoCl_2 \cdot L_2$ (**5a—c**) (L_2 are diamines **1a—c**). According to elemental analysis, each of the three complexes contains one diamine molecule and, presumably, they have a tetrahedral geometry. Thus, X-ray diffraction data[15] imply that the $CoCl_2 \cdot$ *N*,*N*,*N*′,*N*′-tetramethylpropane-1,3-diamine has a tetrahedral structure.



$CoCl_2 \cdot L_2$ (**5a—c**)

In the IR spectrum of complex **5a**, the N—H stretching bands (3320, 3270, and 3210 cm^{-1}) shift relative to the bands of free diamine **1a** (3360, 3290, and 3190 cm^{-1}, respectively) due to the transfer of the electron density

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 342—347, February, 2005.

1066-5285/05/5402-0348 © 2005 Springer Science+Business Media, Inc.

Table 1. Reduction of acetophenone (**2**) with sodium borohydride in the CoX_2 + **1a—d** system (X = Cl, OTf) and in the presence of complexes **5a—c**[a]

Run	Catalyst	Solvent	Modifying agent	t^b/h	Substrate : Co	Conversion (%)	*ee* (*S*) (%)
1	—	$CHCl_3$	2 EtOH	24	—	1	—
2	—	THF	2 EtOH	24	—	1	—
3	$CoCl_2$ + 2 **1a**	$CHCl_3$	—	48	100	27^c	—
4	$CoCl_2$ + 2 **1a**	$CHCl_3$	10 EtOH	48	100	20^c	7
5	$Co(OTf)_2$ + **1a**	EtOH	—	24	80	100^c	8
6	$Co(OTf)_2$ + 2 **1a**	EtOH	—	24	80	100	10
7	**5a**	$CHCl_3$	10 Pr^{i}OH	24	80	21^c	9
8	**5a**	$CHCl_3$	10 Pr^{i}OH + 1 MeOH	24	80	23^c	13
9	**5b**	$CHCl_3$	10 Pr^{i}OH	24	80	21	15
10	**5b**	$CHCl_3$	10 Pr^{i}OH + 1 MeOH	24	80	25	18
11	$CoCl_2$ + **1c**	THF	2 EtOH	24	100	1	—
12	$CoCl_2$ + 2 **1c**	EtOH	—	8	100	100^c	2
13	$CoCl_2$ + **1c**	$CHCl_3$	2 MeOH	24	120	14^c	12
14	$CoCl_2$ + **1c**	$CHCl_3$	2 EtOH	24	120	14^c	19
15	**5c**	$CHCl_3$	2 EtOH	24	80	21^c	20
16	$CoCl_2$ + 2 **1c**	$CHCl_3$	10 EtOH	24	120	24^c	21
17	**5c**	$CHCl_3$	10 Pr^{i}OH	24	80	19^c	21
18	**5c**	$CHCl_3$	10 Pr^{i}OH + 1 MeOH	24	80	23^c	24
19	$Co(OTf)_2$ + **1d**	EtOH	—	8	55	100^c	0
20	$Co(OTf)_2$ + **1d**	THF	2 EtOH	8	55	100^c	0
21	$CoCl_2$ + **1d**^{d}	THF	2 EtOH	8	55	100^c	0
22	$CoCl_2$ + **1d**	THF	1 EtOH + 1 MeOH	8	55	100^c	0
23	$CoCl_2$ + **1d**	$CHCl_3$	2 EtOH	8	120	30^c	0

[a] $C_{Co} = 10$ mmol L^{-1}, $V = 10$ mL, Na : Co = 80—120, −20 °C.

[b] Reaction duration.

[c] A black precipitate is formed.

[d] The duration of catalyst formation is 3 days.

from nitrogen atoms to the metal atom. The ν(NH) stretching band for complex **5b** is located at 3190 cm^{-1}, *i.e.*, at a lower frequency than the absorption bands of secondary diamine **1b** (3270 and 3320 cm^{-1}).

The isolated complexes and the catalytic systems obtained *in situ* from diamines **1a—d** and anhydrous $CoCl_2$ and $Co(CF_3SO_3)_2$ were studied in the reduction of acetophenone (**2**) with sodium borohydride in EtOH, $CHCl_3$, and THF (Table 1). Preliminarily, it was shown that in the absence of a catalyst, the reduction of acetophenone under the reaction conditions proceeds to a low extent (see Table 1, runs *1* and *2*).

Sodium borohydride was modified with alcohols (Scheme 1) in order to decrease its reducing potential and increase the solubility in THF and $CHCl_3$ and to study the effect of the nature of substituents in sodium di- or trialkoxyborohydride on the process enantioselectivity.

Scheme 1

$$NaBH_4 + n\ ROH \longrightarrow NaBH_{4-n}(OR)_n + n\ H_2$$

$n = 2, 3$

The reduction of acetophenone in the presence of complexes **5a—c** affords an excess of (*S*)-(−)-1-phenylethanol, irrespective of the nature of the ligand, the modifier, or the solvent, while in the CoX_2 + **1d** system (X = Cl, TfO), the optical yield of the product is close to zero in all cases. The highest optical yields of the product (*S*)-isomer were obtained for complex **5c** or in a catalytic system containing diamine **1c** (see Table 1, runs *11—18*). The enhancement of the steric hindrance in the modifying alcohol (Me < Et < Pr^i) results in a higher optical yield of the product (see Table 1, runs *13—17*); however, a combination of MeOH and Pr^{i}OH proved to be most efficient (run *18*). The same behavior is observed in the reduction of acetophenone in the presence of complex **5a** (runs *7*, *8*) or **5b** (runs *9*, *10*).

One may expect that diamine **1b** containing three different substituents at each N atom would exert an additional asymmetrizing action in the metal coordination sphere when coordinated to a Co atom due to the appearance of stereogenic N atoms. However, as follows from the experimental data, the process enantioselectivity in the presence of complex **5b** (see Table 1, runs *9* and *10*) does not exceed that attained with complex **5c** (runs *17* and *18*). This might be related to different solubilities of the starting cobalt complexes in $CHCl_3$ and CH_2Cl_2, which decreases in the sequence **5c** > **5b** >> **5a**.

Note that a finely dispersed cobalt-containing precipitate was formed in all experiments, the amount of the precipitate and the precipitation rate being dependent on the nature of the ligand and decreasing in the sequence **1d** > **1a** > **1b** > **1c**. For example, the catalytic system based on complex **5c** remains visually homogeneous for more than 24 h, whereas in the catalytic system based on complexes **5a** or **5d**, precipitation takes place during the first 5 h.

In the case of catalytic systems based on diamine **1d** in which the optical yields are close to zero, the solution turns dark-brown 1—2 min after the introduction of sodium alkoxyborohydride, while 1—2 h later, a black precipitate is formed. This type of behavior of diamine **1d** stimulated us to study the complexation of this compound with $CoCl_2$ in more detail by UV spectroscopy in various solvents.[13] Complexation did not take place in propylene carbonate, dioxane, MeCN, or $CHCl_3$, while in THF, slow complex formation occured through η^6-binding of the diamine phenyl groups to the Co atom rather than through bidentate binding of the lone electron pairs of the diamine N atoms to the metal atom. This fact accounts for the nearly zero enantioselectivity in the $CoCl_2$ + **1d** system in which the traditional seven-membered cobalt diamine chelate is not formed, unlike the catalytic systems containing diamines **1a—c**. We could not isolate the individual complex $CoCl_2 \cdot$ **1d**. The maintenance of the $CoCl_2$ + **1d** system for 3 days in THF does not lead to a better outcome (see Table 1, run *21*).

The results of reduction of esters **3** and **4** to methyl ester of *N*-acetylphenylalanine ($PhCH_2CH(NHCOMe)COOMe$) or to dimethyl α-methylsuccinate ($MeOCOCH_2CH(Me)COOMe$), respectively, catalyzed by complex **5** are summarized in Table 2.

The greatest *ee* value (31%) of dimethyl (*S*)-α-methylsuccinate, which is formed quantitatively in all cases in DMF, was attained in the reduction of ester **4** with nonmodified $NaBH_4$ in the presence of complex **5c**. A lower enantioselectivity was found in the presence of complex **5a**. The *ee* value decreases when substrates are reduced in the presence of complexes **5a** and **5c** with $NaBH_4$ modified by alcohols with an ROH : Na ratio of 2 : 1. The sign of the asymmetric induction for complex **5a** is opposite to that observed with complexes **5b** and **5c**. The reduction of ester **3** is accompanied by the formation of a suspension of "colloid" cobalt, which may be responsible for low optical yields.

Study of noncatalyzed reduction of substrates **3** and **4** with sodium alkoxyborohydrides showed that the former is barely reduced over a period of 24 h. Conversely, for substrate **4**, containing a terminal C=C bond, the rates of the catalyzed and noncatalyzed processes are commensurable, which accounts for relatively low *ee* values.

The reduction of diester **4** in the presence of complexes **5b,c** not complicated by the noncatalyzed process

Table 2. Reduction of esters **3** and **4** with sodium borohydride in the presence of cobalt complexes $CoCl_2 \cdot L_2$ in DMF at 20 °C[a]

Run	Ligand	Modifying agent (ROH : Na)	Substrate (substrate : Co)	*t*[b]/h	Conversion (%)	*ee* (%)
1	—	Pr^{i}OH (1) + MeOH (1)	**4**	9	100	—
2	—	Pr^{i}OH (1) + MeOH (1)	**3**	24	0	—
3	**1a**	—	**4** (63)	11	100	16 (*R*)
4	**1a**	MeOH (2)	**4** (63)	9	100	4 (*R*)
5	**1b**	Pr^{i}OH (1) + MeOH (1)	**4** (63)	10	100	2 (*S*)
6	**1c**	—	**4** (63)	11	100	31 (*S*)
7	**1c**	MeOH (2)	**4** (63)	9	100	3 (*S*)
8	**1c**	Pr^{i}OH (1) + MeOH (1)	**4** (63)	9	100	18 (*S*)
9[c]	**1b**	Pr^{i}OH (1) + MeOH (1)	**4** (40)	72[d]	94	30 (*S*)
10[c]	**1c**	Pr^{i}OH (1) + MeOH (1)	**4** (40)	120[d]	75	38 (*S*)
11[e]	**1c**[f]	Pr^{i}OH (1) + MeOH (1)	**3** (46)	8[d]	46	15 (*S*)
12[e]	**1a**[g]	Pr^{i}OH (1) + MeOH (1)	**3** (16)	20[d]	23	8 (*S*)
13[e]	**1b**[h]	Pr^{i}OH (1) + MeOH (1)	**3** (50)	10[d]	22	16 (*S*)

[a] $C_{Co} = 2$ mmol L^{-1}, $V = 25$ mL, $NaBH_4$: substrate = 2.
[b] Reaction duration.
[c] In $CHCl_3$.
[d] A black precipitate is formed.
[e] In DMF : toluene = 6 : 1.
[f] $NaBH_4$: substrate = 1.3.
[g] $NaBH_4$: substrate = 4.
[h] $C_{Co} = 1$ mmol L^{-1}.

could be studied in $CHCl_3$. The noncatalyzed reduction with sodium alkoxyborohydrides does not proceed in this solvent and the solubility of these complexes is satisfactory. The hydrogenation rate markedly decreases but the optical yield increases to 38%, the sign of asymmetric induction being retained (see Table 2, runs *9* and *10*). For both ligands, brown solutions are formed and then a black solid precipitates, these changes being faster in the presence of complex **5b**.

The intermediate formation of hydrides MH has been suggested[16] in the development of a method for the preparation of pure Co and Ni powders by the reaction of metal chlorides MCl_2 with complex hydrides $M'H \cdot [BR_n(OR')_{3-n}]$ (M' = Li, Na; R, R' = Alk; n = 1—3) (Scheme 2).

Scheme 2

$$MX_2 + 2\,M'(BR_3H) \xrightarrow[-2\,M'X]{} (M...H...BR_3) \longrightarrow$$

$$\longrightarrow [MH] + BR_3 \longrightarrow M + 0.5\,H_2$$

Evidently, in the presence of electron-donating ligands able to stabilize the Co—H bond,[17] the complex cobalt hydride can add the substrate to give the cobalt alkyl derivative, which undergoes hydrogenolysis by one or another mechanism, for example, with sodium alkoxyborohydride.

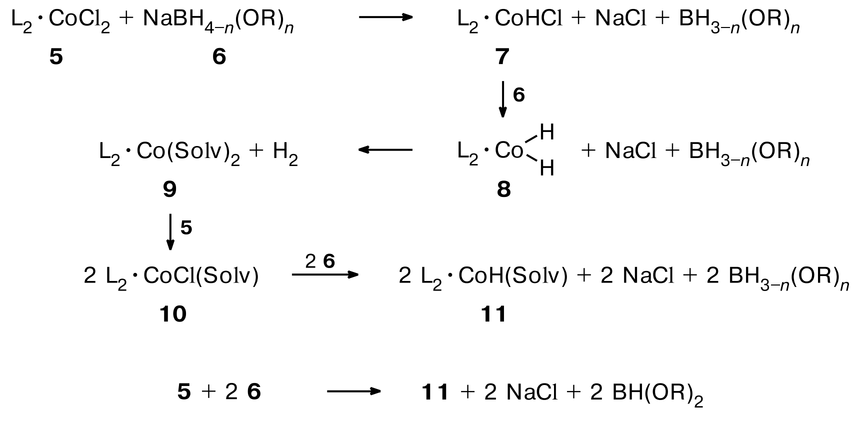
It should be noted that the reactions of complexes **5** with sodium alkoxyborohydrides **6** (Scheme 3) are accompanied by evolution of molecular hydrogen. The formation of the catalytically active cobalt hydride can be represented as two consecutive replacements of Cl atoms by H atoms giving rise to unstable dihydride **8**, which rapidly decomposes with hydrogen evolution to give zerovalent cobalt complex **9**. This complex, in turn, undergoes disproportionation with another molecule of the starting dichloride complex **5**. The resulting Co^I monochloride **10** can undergo an exchange reaction with $NaBH_{4-n}(OR)_n$ to yield active cobalt hydride **11**. According to the last equation (see Scheme 3), the reduction of one molecule of complex **5** requires two molecules of modified sodium borohydride **6**.

In the absence of strong π-acceptor ligands, the probability of formation of colloid particles based on zerovalent cobalt complexes is especially high in $CHCl_3$, which is unable to stabilize complex **9** in solution. Conversely, hydrogenation of diester **4** in DMF, which is a good complexing agent, barely gives any precipitate. When toluene is used as a co-solvent, the precipitate is formed more slowly, which attests to insertion of toluene molecules as π-ligands into the coordination sphere of the transition metal.[18] This retards aggregation of Co^0 particles to give larger particles resulting in precipitation.

According to powder X-ray diffraction data contained in the PDF data base,[19] the "colloid" cobalt precipitate incorporates a minor amount of NaCl. Cobalt metal or cobalt compounds with boron (Co_2B and CoB) cannot be detected, probably, as they are amorphous to X-rays (particle size <10 Å).[20] According to scanning electron microscopy, the precipitate is an amorphous uniform structureless material in which it is difficult to distinguish a base unit. After annealing under argon for 6 h at 450 °C, the sample becomes more crystalline, and clear lines representing four diffraction maxima, which correspond to cubic elemental cobalt (β-Co), appear in the X-ray diffraction patterns. The particle size calculated using the Selyakov—Sherer formula equals ~318 Å.[21]

Presumably, the reduction of substrates with the given catalytic systems is a complex multipathway process involving both homogeneous chiral Co^I diamine hydride

Scheme 3



Solv is solvent

complexes (possibly, only at an early stage) and microheterogeneous cobalt-containing particles, which make a certain contribution to hydrogenation. In the absence of a sufficient amount of stabilizing ligands and surfactants, the latter particles coalesce and precipitate. The fact that this precipitate contains some nitrogen, hydrogen, and carbon even after thorough washing and drying suggests that colloid particles can be modified by chiral diamine ligands or their fragments. This can also influence the enantioselective reduction of the substrates.

The question of whether the reduction of aryl ketones and dehydro acids in the presence of cobalt diamine is a homogeneous or a heterogeneous process would be tackled in our further studies.

Experimental

Chloroform, CH_2Cl_2, toluene, DMF, and acetophenone were purified and dehydrated by standard procedures and distilled under argon.

IR spectra were recorded on an IKS-29 instrument in KBr. GLC analysis was performed on an LKhM-80 chromatograph (2 m × 3 mm columns, 5% SE-30 on Chromaton N-AW-DMCS, heat conductivity detector, helium as the carrier gas). The specific rotation was measured on a Polamat A instrument (*c* 2—30, MeOH or $CHCl_3$) at $\lambda = 546$ nm. The powder X-ray diffraction analysis of solid precipitates was performed on a DRON-3M X-ray diffractometer (Cu-Kα radiation). The micrographs of the "colloid" cobalt were taken at the Instrument Center "Electron Microscopy" of the Limnological Institute of the Siberian Branch of the Russian Academy of Sciences on a 287-fold Philips´ SEM 525-M scanning electron microscope.

Diamines **1a—d** were synthesized as described previously.[12,13] Diamine complexes **5** were prepared by a known procedure[15] and dried for 8 h *in vacuo* (3 Torr) at 60—70 °C. Complex **5a** precipitated from suspension of $CoCl_2$ and a solution of the starting diamine without passing to a CH_2Cl_2 solution, whereas complexes **5b,c** are soluble in CH_2Cl_2. Complex **5b** was obtained as a dark-blue oil from which crystals were formed on storage in the cold for several days.

Dichloro[(4*S*,5*S*)-2,2-dimethyl-4,5-bis(aminomethyl)-1,3-dioxolane]cobalt(II) (5a). Yield 81.0%, m.p. 230—232 °C. Found (%): C, 27.92; H, 5.77; Cl, 25.53; N, 9.23. $C_7H_{16}Cl_2CoN_2O_2$. Calculated (%): C, 28.99; H, 5.56; Cl, 24.45; N, 9.66. IR, ν(N—H)/cm^{-1} (the absorption bands of the free ligand are given in parentheses): 3210 (3190), 3270 (3290), 3320 (3360).

Dichloro[(4*S*,5*S*)-2,2-dimethyl-4,5-bis(methylaminomethyl)-1,3-dioxolane]cobalt(II) (5b). Yield 66.5%, m.p. 97—98 °C. Found (%): C, 35.00; H, 6.83; Cl, 21.37; N, 8.93. $C_9H_{20}Cl_2CoN_2O_2$. Calculated (%): C, 33.98; H, 6.34; Cl, 22.29; N, 8.81. IR, ν(N—H)/cm^{-1} (the absorption bands of the free ligand are given in parentheses): 3190 (3273, 3328).

Dichloro[(4*S*,5*S*)-2,2-dimethyl-4,5-bis(dimethylaminomethyl)-1,3-dioxolane]cobalt(II) (5c). Yield 70.8%, m.p. 166—168 °C. Found (%): C, 37.93; H, 7.22; Cl, 21.42; N, 7.71. $C_{11}H_{24}Cl_2CoN_2O_2$. Calculated (%): C, 38.17; H, 6.99; Cl, 20.48; N, 8.09.

Methyl α-acetamidocinnamate (**2**) was prepared by a known procedure,[22] m.p. 120—121 °C. Dimethyl itaconate (**3**) was synthesized by refluxing itaconic acid in MeOH with some HCl for several days. The white crystals that precipitated on cooling were recrystallized from MeOH, m.p. 38 °C.

Modification of sodium borohydride with alcohols (general procedure). A modifying alcohol (MeOH, EtOH, Pr^{i}OH) (4—20 mmol) or 2 mmol of each alcohol was added to a suspension of $NaBH_4$ (0.077 g, 2 mmol) in 15 mL of $CHCl_3$ (EtOH, THF) or in 5 mL of DMF in the reduction of esters of dehydro acids, and the mixture was stirred for 30 min at ~20 °C under argon.

Reduction of acetophenone (2) (general procedure). A cooled solution of complexes **5a—c** (0.02—0.05 mmol) and acetophenone (**2**) (0.5—1 mL) in 9—9.5 mL of a solvent ($CHCl_3$, EtOH, THF) was slowly added in an argon flow to a solution of modified $NaBH_4$ cooled to −20 °C. The resulting brown solution was evacuated to remove the hydrogen evolved and stirred using a magnetic stirrer for 24—48 h at −20 °C. The degree of conversion was determined by GLC analysis of the reaction mixture. The product was separated from the catalyst and unreacted acetophenone by vacuum distillation. The optical yield (*ee*) was determined for the highest-boiling fraction with the lowest content of acetophenone (≤10% according to GLC) as the ratio of the specific rotation calculated with allowance for the content of 1-phenylethanol to the published value for 1-phenylethanol (in MeOH) by a previously described procedure.[14]

The reduction of esters of dehydro acids 3 and 4. A solution of complexes **5a—c** (0.02—0.05 mmol) and ester **3** or **4** (1.5—4 mmol) in 10 mL of DMF or a $CHCl_3$—toluene mixture (6 : 1) was slowly added to 15 mL of a solution of modified $NaBH_4$ in DMF or $CHCl_3$. After degassing, the mixture was stirred for 9—10 h (in the case of ester **3**) or for 24—48 h (in the case of ester **4**). To terminate the reaction, 1—2 mL of a saturated solution of NH_4Cl was added. After quenching of the active components of the reaction mixture, 50 mL of CH_2Cl_2 and 50 mL of water were added, the organic layer was washed with water several times, dried with anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The chemical yield of ester **3** was determined by GLC, and that of ester **4**, by ^{1}H NMR spectroscopy. The products were isolated and purified by column chromatography on silica gel (elution with hexane—AcOEt, 9 : 1).

The optical yields were calculated relative to the specific rotation of dimethyl *R*-(+)-α-methylsuccinate ($[\alpha]_{546}^{20}$ +7.7 (neat)) calculated using the Drude equation based on the following data: $[\alpha]_D^{20}$ +6.44 (neat), $K = 3.15 \cdot 10^6$, $\lambda_0 = 204$ nm,[23] $[\alpha]_D$ +4.8 (*c* 2.9, $CHCl_3$);[24] methyl *S*-(+)-*N*-acetylphenylalanine ($[\alpha]_{546}^{20}$ +19.3 (*c* 2.0, MeOH), $[\alpha]_D^{20}$ +16.4 (*c* 2.0, MeOH))[25]; *S*-(−)-1-phenylethanol ($[\alpha]_D^{20}$ −45.0 (*c* 5, MeOH))[26] and *R*-(+)-1-phenylethanol ($[\alpha]_{546}^{25}$ +43.9 (neat)).[27]

The precipitate of the "colloid" cobalt was separated by decanting off the catalyzate solution, washed many times with DMF and $CHCl_3$, and dried *in vacuo* (5 h, 100 °C, 1 Torr). Found (%): C, 6.15; H, 2.30; Cl, 2.52; N, 1.89; ash, 74.91.

The authors are grateful to E. V. Likhoshvai (Limnological Institute of the Siberian Branch of the Russian Academy of Sciences) for taking images by scanning electron microscopy.

References

1. S.-K. Chang, *J. Org. Chem.*, 1979, **44**, 1914.
2. A. Kasahara and T. J. Hongu, *Nippon Kagaku Zasshi*, 1965, **86**, 1343.
3. A. Rusina, H. P. Schröer, and A. A. Vlček, *Z. Anorg. Allg. Chem.*, 1967, **351**, 275.
4. A. Fârkas, U. Luca, N. Morar, and O. Piringer, *Z. Phys. Chem.*, 1968, **58**, 87.
5. U. Leutenegger, A. Madin, and A. Pfaltz, *Angew. Chem.*, 1989, **101**, 61.
6. P. Matt and A. Pfaltz, *Tetrhedron: Asymmetry*, 1991, **2**, 691.
7. M. Misun and A. Pfaltz, *Helv. Chim. Acta*, 1996, **79**, 961.
8. K. D. Sugi, T. Nagata, T. Yamada, and T. Mukaiyama, *Chem. Lett.*, 1996, 1081.
9. T. Yamada, T. Nagata, T. Ikeno, Y. Ohtsuka, T. Sagora, and T. Mukaiyama, *Inorg. Chim. Acta*, 1999, **296**, 86.
10. T. Nagata, K. Yororu, T. Yamada, and T. Mukaiyama, *Angew. Chem.*, 1995, **107**, 2309.
11. K. D. Sugi, T. Nagata, T. Yamada, and T. Mukaiyama, *Chem. Lett.*, 1997, 493.
12. B. A. Shainyan, M. V. Ustinov, and L. O. Nindakova, *Zh. Organ. Khim.*, 2001, **37**, 1838 [*Russ. J. Org. Chem.*, 2001, **37**, 1757 (Engl. Transl.)].
13. B. A. Shainyan, L. O. Nindakova, M. V. Ustinov, N. N. Chipanina, and L. V. Sherstyannikova, *Zh. Organ. Khim.*, 2002, **38**, 1862 [*Russ. J. Org. Chem.*, 2002, **38**, 1802 (Engl. Transl.)].
14. L. O. Nindakova, B. A. Shainyan, and L. N. Belonogova, *Zh. Organ. Khim.*, 2003, **39**, 1553 [*Russ. J. Org. Chem.*, 2003, **39** Engl. Transl.)].
15. D. A. Handley, P. B. Hitchcock, T. H. Lee, and G. J. Leigh, *Inorg. Chim. Acta*, 2001, **314**, 14.
16. H. Bonneman, W. Brijoux, and T. Joussen, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 273.
17. Yu. N. Kukushkin, *Reaktsionnaya sposobnost´ koordinatsionnykh soedinenii* [*Reactivity of Coordination compounds*], Khimiya, Leningrad, 1987, 288 pp (in Russian).
18. F. K. Shmidt, V. V. Sarayev, Y. S. Levkovskii, V. G. Lipovich, V. A. Gruznykh, G. V. Ratovskii, T. V. Dmitrieva, and L. O. Nindakova, *React. Kinet. Catal. Lett.*, 1979, **10**, 195.
19. *Powder Diffraction Fil. ICPDS*, Philadelphia (USA), 1977, **5**, 0685.
20. *Sovremennaya kristallografiya* [*Modern Crystallography*], Ed. V. K. Vanshtein, A. A. Chernov, and L. A. Shuvalov, Nauka, Moscow, 1979, **1**, 401 pp. (in Russian).
21. A. I. Kitaigorodskii, *Rentgenostrukturnyi analiz melkokristallicheskikh i amorfnykh tel* [*X-Ray Diffraction Analysis of Finely Crystalline and Amorphous Solids*], Gos. Izd. Tekhn.-Teoret. Lit., Moscow—Leningrad, 1952, 588 pp. (in Russian).
22. *Organic Syntheses*, Ed. A. Blatt, J. Wiley and Sons, New York—London, 1946, **2**.
23. V. A. Pavlov, E. N. Rassadkina, E. I. Karpeiskaya, G. V. Chel´tsova, L. N. Kaigorodova, and E. I. Klabunovskii, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1980, 1087 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29**, 794 (Engl. Transl.)].
24. R. Rossi, P. Diversi, and G. Ingrosso, *Gazz. Chim. Ital.*, 1968, **98**, 1391.
25. B. D. Vineyard, W. S. Knowles, M. J. Sabasky, G. L. Bachman, and D. J. Weinkauff, *J. Am. Chem. Soc.*, 1977, **99**, 5946.
26. S. Gladiali, G. Chelucci, F. Soccolini, G. Delogu, and G. Chessa, *J. Organomet. Chem.*, 1989, **370**, 285.
27. G. Zassinovich, R. Bettella, G. Mestroni, N. Bresciani-Pahor, S. Geremia, and L. Randaccio, *J. Organomet. Chem.*, 1989, **370**, 187.

Received July 9, 2003;
in revised form April 21, 2004