A novel type of catalysts for the asymmetric C—C bond formation based on chiral stereochemically inert cationic Co^{III} complexes

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Schiff bases derived from (1*R*,2*R*)-1,2-diaminocyclohexane and 1 eq. of salycylic (or substituted salycylic) aldehyde form stereochemically inert positively charged chiral octahedral Co^{III} complexes of Δ-configuration with the stereoselectivity approaching 100%. To evaluate the calatylic activity and stereoinduction of the resulting complexes with various counteranions in the outer sphere, a model reaction of trimethylsilyl cyanide addition to benzaldehyde was used. *O*-trimethylsilylmandelonitrile formed in the process had an enantiomeric purity up to 27%. Complexes with F^- counterion showed high catalytic activity.

Key words: asymmetric catalysis, metal complex catalysis, reaction of the trimethylsilylcyanation of aldehydes.

Synthesis of enantiomerically pure organic compounds, particularly pharmaceutical forms, is a problem of extreme importance in chemical technology (see Refs 1 and 2). From the economical viewpoint, catalytic methods of asymmetric synthesis are the most attractive (see Refs 1 and 2). For this reason, the formation of C—C bond using asymmetric catalysts, is still one of the most popular fields of investigations both in fundamental and in applied chemistry. Particular attention of scientists is directed to chiral metal complexes (Lewis acids), as asymmetric catalysts of these reactions (see Ref. 3). A conceptional framework of this catalysis is very simple. A strong coordinative interaction between a metal ion and a substrate provides the energy sufficient for the further orientation of the substrate in the position which is optimal for an asymmetric reaction. This orientation results from the repulsive force (nonbonding interactions) of the chiral ligand groups. However, it is the strong interaction between a metal and an intermediate product, that sufficiently decreases the total rate of the reaction rendering the catalytic effect either impossible or hindered. In this connection, during the last decade, considerable advances have been made in the novel area of asymmetric catalysis — an asymmetric organic catalyis (see Refs 4 and 5). Catalysis of this type is based on the use of chiral organic molecules as catalysts, providing an orientation of a substrate in the space due to the few bonding weak interactions with the catalyst groups. Such catalysts are represented by positively charged chiral quaternary ammonium salts (see Refs 6 and 7), which have originally been obtained from Cinchona type alkaloids (see Ref. 7). Brønsted acids (see Refs 8 and 9) and their negatively charged conjugated bases obtained from 1,1′-bi-2-naphtol (BINOL) derivatives also belong to such catalysts (see Ref. 10). Unfortunately, with rare exception, the effectiveness of organic asymmetric catalysis does not reach the average level of catalysts based on Lewis acids, particularly, because of the limited set of chiral frameworks of organic catalyts. Thus, the organic framework of the Cinchona type alkaloids is difficult to modify (see Ref. 7), and the environment of the acid group of phosphorus acids based on BINOL needs to be sterically overloaded to reach a high asymmetric induction (see Ref. 10), which results naturally in the loss of their catalytic activity. Obviously, a new approach to construct asymmetric catalysts is required that serves to develop asymmetric catalysts devoid of disadvantages of the currently available catalysts. An attempt to develop this approach is described in the present work.

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Results and Discussion

A novel catalyst suggested for the asymmetric synthesis are positively charged Co^{III} complexes (Fig. 1) with octahedral surroundings that are stereochemically inert and possess both central and meridional chirality.

Positively charged hydrophobic metal complexes **1**—**3** have been obtained according to the specially developed procedure using the assembly from building blocks (Scheme 1). Modules constituting the chiral metal complex cation represent substituted salycylic aldehydes, (1*R*,2*R*)-1,2-diaminocyclohexane and the cobalt salt.

The synthesis of compounds **1**—**3** comprises several steps (see Scheme 1). At the first step the Schiff base derived from (1*R*,2*R*)-1,2-diaminocyclohexane and salycylic (or substituted salycylic) aldehyde is obtained, and at the second step, two molecules of the Schiff base and the cobalt salt yield the target complex. At the final step, the counterion may be changed readily for any other one by ion-exchange chromatography; in our case Cl^-, F^- and BF_4^- counterions were used. Complexes may be formed as a mixture of two diastereomers, Λ(*R*,*R*) and Δ(*R*,*R*) (see Fig. 1). However, the stereoselectivity of the resulting complexes is so high that the Δ-isomer is formed in a minor amount, and attempts to isolate it as an individual compound failed.

Complexes **1**—**3** obtained are dark-brown crystal compounds fairly soluble in ethyl alcohol and polar aprotic solvents.

The structure of compounds **1**—**3** has been confirmed by the elemental analysis data. Since complexes **1**—**3** are diamagnetic (the configuration of the Co^{III} ion is $4s^23d^6$), they were also characterized by the NMR ^1H spectroscopy data. Spectra of the compounds **1**—**3** show very similar set of signals corresponding to the expected one for the complexes having C_2-symmetry, and the significant differences are observed only among the chemical shifts of the NH_2-group protons. In the case of chlorine as a counterion, the signal of a proton of the amino group is located in the range of 6.40—6.75 ppm, and that of the second proton — in the range of 1.45—2.09 ppm. When a fluoride anion presents a counterion in the outer complex sphere, the signal of the first proton of amino group shifts to the range of 2.53—2.90 ppm, and the signal of the other proton remains in the same interval as for the chloride anion, i.e. between 1.45—2.09 ppm. This implies the hydrogen bonding of fluoride anion

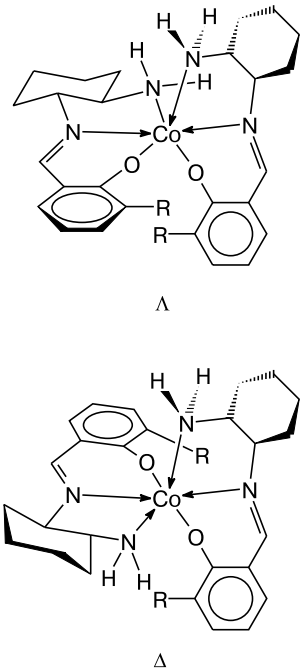
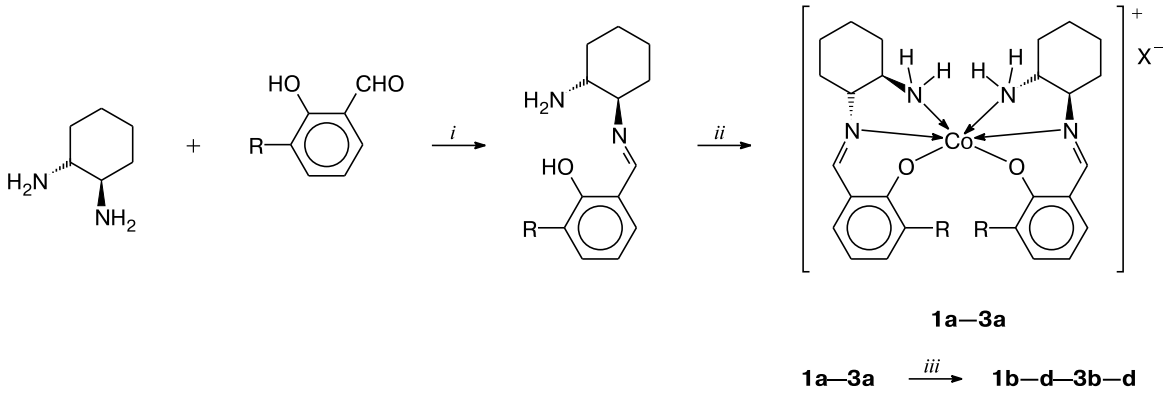


Fig. 1. Stereochemically inert, chiral, octahedral, positively charged Co^{III} complexes.

Scheme 1



R = H (**1**), OCH_3 (**2**), CH_2—CH=CH_2 (**3**); X = HCO_3^- (**a**), Cl^- (**b**), F (**c**), BF_4^- (**d**)

Reagents and conditions: *i*. $CHCl_3$, 0 °C; *ii*. $Na_3[Co(CO_3)_3]\cdot 3H_2O$, EtOH, Δ; *iii*. ion-exchange chromatography.

with the complex to be more strong than that of the chloride anion.

To ascribe the configuration of complexes based on the substituted salycylic aldehydes, a NMR experiment using NOESY procedure for the compound [Λ-**3**]$^+$Cl$^-$ (Fig. 2) derived from (1*R*,2*R*)-1,2-diaminocyclohexane and 3-allyl-2-hydroxybenzaldehyde has been performed. Figure 2 shows the cross peak observed between the *pro-R*-proton of the amino group of the cyclohexane diaminic moiety and the proton of the >CH—N= moiety, which evidences their spatial proximity. Such a mutual disposition of these moieties for the complex based on (1*R*,2*R*)-1,2-diaminocyclohexane may occur only in the isomer of Λ-configuration.

Absolute configurations of complexes [Λ-**3**]$^+$Cl$^-$ and [Λ-**1**]$^+$F$^-$ were confirmed by the X-ray diffraction method with their structures shown in Figures 3 and 4, correspondingly.

Referring to Figure 3, one chlorine anion forms four hydrogen bonds with protons of NH_2-groups of both complexes, the NH···Cl bond lengths ranging from 3.24—3.26 Å.

In the structure of [Λ-**1**]$^+$F$^-$ the fluorine anion is bonded to a cation (see Fig. 4), where the coordination sphere of the anion includes two chloroform molecules forming additional hydrogen bonds with the fluorine ion in addition to the metal complex cation coordinated by two protons of NH-groups of cyclohexanediaminic moieties, and the NH···F bond lengths are in the range from 2.65 to 2.7 Å. The cobalt complexes in the crystal are assembled in the infinite coupled chains due to the cation-anion interactions.

Basing on the analysis of hydrogen bond lengths in the complexes [Λ-**1**]$^+$F$^-$ and [Λ-**3**]$^+$Cl$^-$, one may state that these bonds are sufficiently strong (see Refs 11—14) and, correspondingly, the complexes *per se* may catalyze a wide range of asymmetric chemical reactions, like chiral thioureas (see Ref. 15).

The presence of strong hydrogen bonds between the counterions [Λ-**3**]$^+$Cl$^-$, [Λ-**1**]$^+$F$^-$ and protons of the coordinated amino groups suggests that the latter have a sufficient Brønsted acidity and the resulting cationic complexes are metal-activated organic Brønsted acids (see Ref. 16). Correspondingly, they may be considered as a new type of chiral organocatalysts of modular structure. To support this proposal, these complexes were used as catalysts of the asymmetric C—C bond formation reactions.

Condensation of trimethylsilyl cyanide with benzaldehyde was chosen as a model reaction (Scheme 2). According to the current ideas, this reaction is catalyzed both by Bronsted and Lewis acids and bases. The acids activate the aldehyde carbonyl group, whereas the bases activate

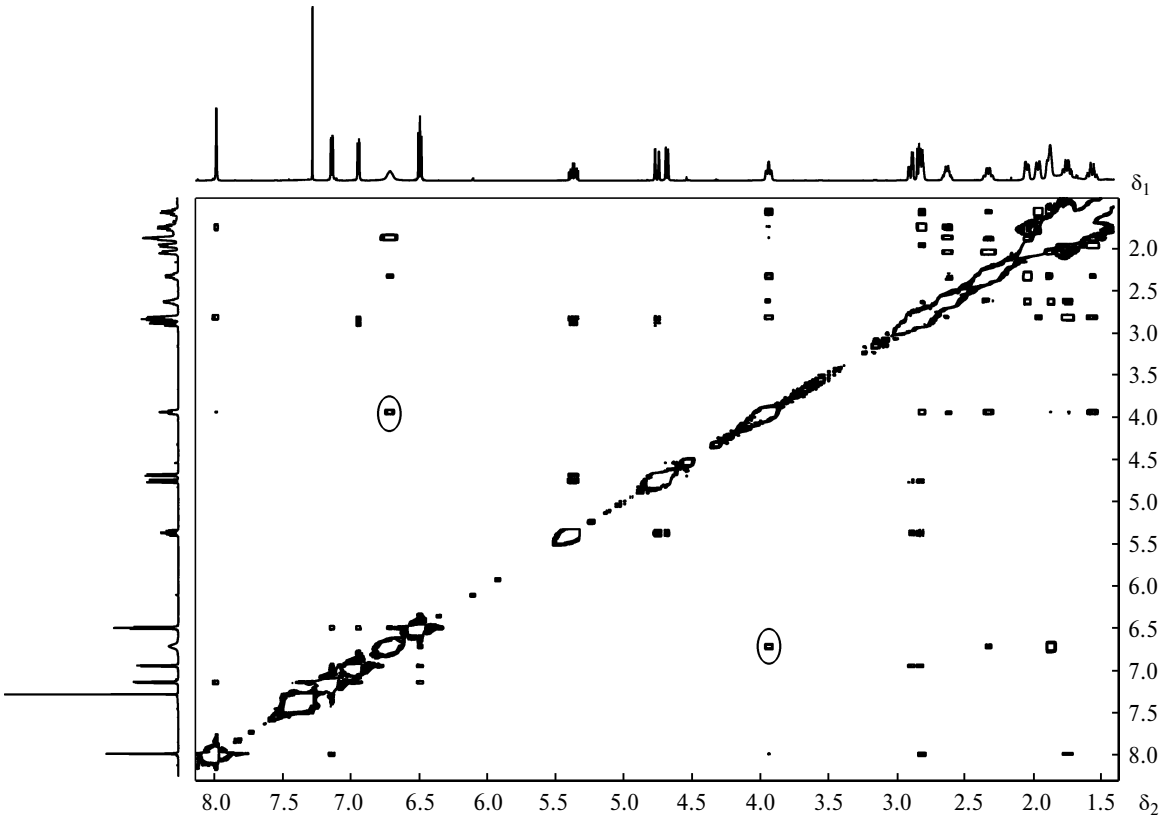


Fig. 2. Two-dimensional NMR experiment using NOESY procedure for complexes [Λ-**3**]$^+$Cl$^-$. Cross peaks between the *pro-R*-protones of the amino group of the cyclohexane diamine moiety and the protone of >CH—N= moiety are encircled with oval.

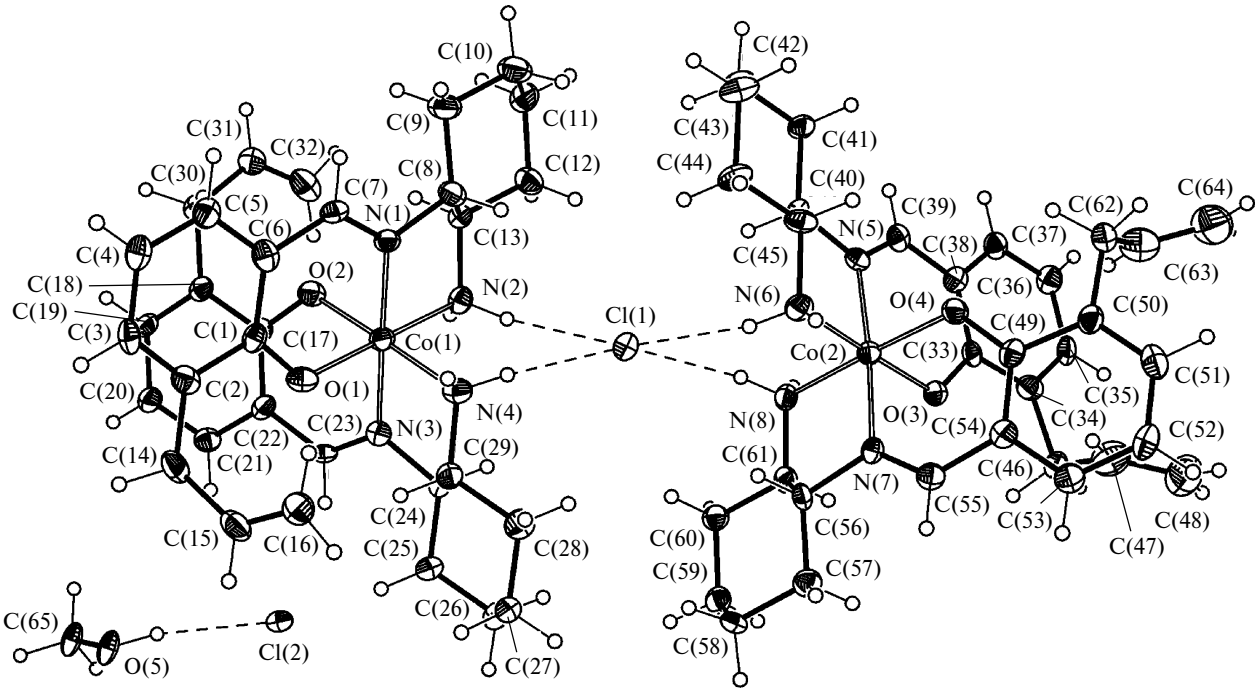


Fig. 3. Structure of the complex $[\Lambda\text{-}\mathbf{3}]^{+}Cl^{-}$ according to the X-ray diffraction data.

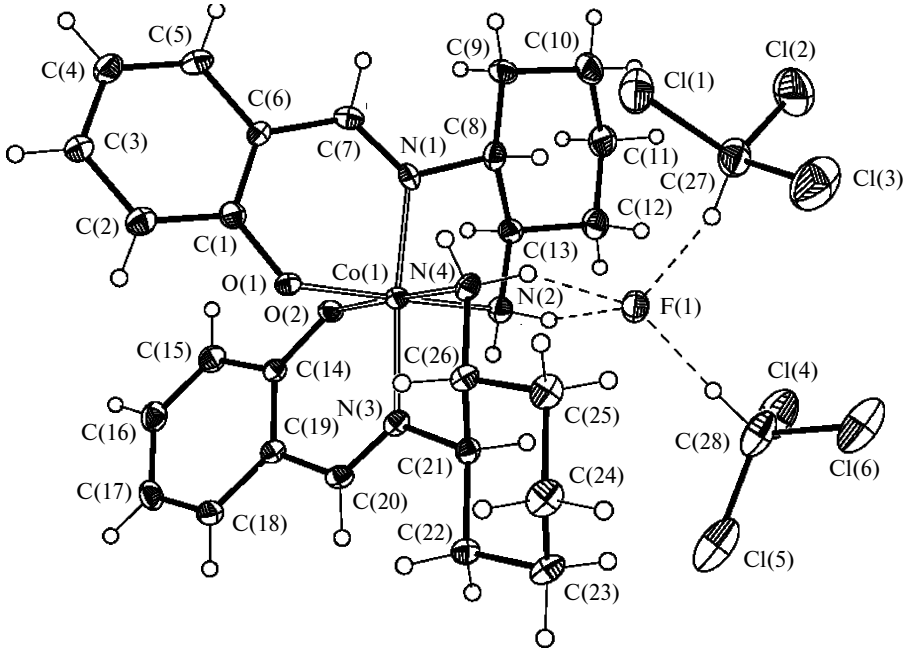
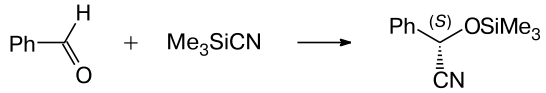


Fig. 4. Structure of the complex $[\Lambda\text{-}\mathbf{1}]^{+}F^{-}$ according to the X-ray diffraction data.

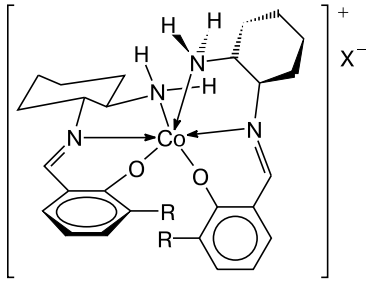
trimethyl silyl cyanide (TMSCN) molecule, forming pentacoordinated silicon compound wherein the cyanide-ion have an additional mobility (see Ref. 17). New complexes were expected to be effective catalysts for the reaction as Brønsted acids, and an outer-sphere anion would be a base, activating TMSCN. Thus, the complexes could be bifunctional catalysts comprising both basic and acidic groups in a molecule.

Reaction of trimethylsilylcyanation of benzaldehyde was performed with 2.5 mol.% of the catalyst at room temperature. The regularities of the solvent influence on the chemical and enantioselective yield was studied using

Scheme 2



Reagents and conditions: catalysts are compounds **1**—**3** (2 mol.%), CH_2Cl_2, 25 °C, Ar.



1—3

X = Cl^-, F^-, BF_4^-
R = H (**1**), OCH_3 (**2**), CH_2—CH=CH_2 (**3**)

the complex $[\Lambda\text{-}\mathbf{3}]^+Cl^-$ as a catalyst. A comparison of CD spectra of $[\Lambda\text{-}\mathbf{3}]^+X^-$ (X^- = HCO_3^-, Cl^- и F^-) complex showed that the spectra did not change with the anion (Fig. 5). This indicates that the counteranion has essentially no influence on the conformations of the chelate rings in complexes in solution.

In all solvents except for chloroform, the complex has proved to be an effective catalyst for the addition reaction of TMSCN and PhCHO (Table 1). However, as one could expect, in basic solvents capable of forming hydrogen bonds with protons of the complex amino groups (MeCN and THF), the asymmetric induction was significantly less than in aprotic solvents. In terms of yield — enantiomeric purity, the best solvent to perform this reaction proved to be CH_2Cl_2, which was used in all the following experiments.

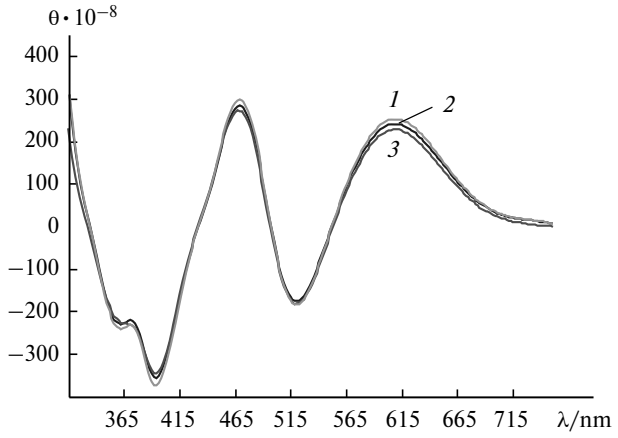


Fig. 5. CD spectra for complexes $[\Lambda\text{-}\mathbf{3}]^+Cl^-$ (*1*), $[\Lambda\text{-}\mathbf{3}]^+F^-$ (*2*) and $[\Lambda\text{-}\mathbf{3}]^+HCO_3^-$(*3*).

Table 1. The effect of solvent on the enantiomeric purity and chemical yield of the product of reaction between TMSCN and PhCHO, catalyzed by the cationic complex $[\Lambda\text{-}\mathbf{3}]^+Cl^-$ [a]

Solvent	Yield (%)[b]	Product *ee* (%)[c,d]
CH_2Cl_2	60	27
$CHCl_3$	40	25
MeCN	86	6
Toluene	100	13
THF	100	6
Hexane	100	21

[a] Reaction conditions: PhCHO (26 mg, 0.246 mmol), TMSCN (31.5 mg, 0.17 mmol), catalyst (2 mol.%, 0.00492 mmol), solvent (1 mL), Ar atmosphere, stirring for 3 h.
[b] Yield according to NMR.
[c] Enantiomeric excess (*ee*) was determined using chiral GLC analysis.
[d] The product of *S*-configuration was formed.

The influence of temperature on the process enantioselectivity is insignificant, since *ee* varies from 23 to 27% in the temperature range of −20 to +28 °C. However the influence of substituents in the salycylic aldehyde moiety is highly significant (Table 2). The highest asymmetric induction of 27% has been observed for catalysis by the complex **3**, whereas for the compounds **1** and **2** this value was in the range of 5—13%.

Nearly all complexes obtained were highly active in catalysis, since (*S*)-*O*-trimethylsilyl mandelonitrile was formed in high and, in some cases, in quantitative yield. The absolute configuration was determined from the comparison of the retention times of the complex obtained and a known enantiomer on a chiral column. It was found

Table 2. The effect of substituents in the salycylic aldehyde moiety of complexes **1**—**3** and structure of counterion on the rate and enantioselectivity of reaction of the trimethylsilylation of benzaldehyde[a]

Complex	Complex cation	Counter-anion	*t*/h	Yield (%)	*ee* (%)[b]
1b	$[\Lambda\text{-}\mathbf{1}]^+$	Cl^-	2	57	9
1c	$[\Lambda\text{-}\mathbf{1}]^+$	F^-	2	100	6
1d	$[\Lambda\text{-}\mathbf{1}]^+$	BF_4^-	15	61	13
2b	$[\Lambda\text{-}\mathbf{2}]^+$	Cl^-	3	81	7
2c	$[\Lambda\text{-}\mathbf{2}]^+$	F^-	3	100	5
3b	$[\Lambda\text{-}\mathbf{3}]^+$	Cl^-	3	60	27
3c	$[\Lambda\text{-}\mathbf{3}]^+$	F^-	3	100	20
3c	$[\Lambda\text{-}\mathbf{3}]^+$	F^- [c]	3	100	20
3d	$[\Lambda\text{-}\mathbf{3}]^+$	BF_4^-	3	6	21

[a] Reaction conditions: PhCHO (26 mg, 0.246 mmol), TMSCN (31.5 mg, 0.17 mmol), catalyst (2 mol.%, 0.00492 mmol), solvent CH_2Cl_2 (1 mL), Ar atmosphere, stirring for 3 h.
[b] In all cases mandelonitrile of (*S*)-configuration was formed.
[c] Substrate:catalyst ratio of 500 : 1 was used.

that the catalyst activity depends mainly on the anion structure, decreasing in a series F > Cl > BF_4. Such a dependence corresponds well to the decrease in the counteranion basicity. For example, conjugated acids of these anions, HF и HCl, have pK_a values in dimethylsulfoxide equal to 15 and 1.8, correspondingly (see Refs 18 and 19). Figure 6 compares kinetics of mandelonitrile accumulation in a catalytic reaction in the presence of $[\Lambda\text{-}\mathbf{3}]^+F^-$ and $[\Lambda\text{-}\mathbf{3}]^+Cl^-$ complexes (0.5 mol.%) in CH_2Cl_2 at room temperature. Obviously, fluoride complex is several orders higher in catalytic activity than chloride complex. In this case catalytic activity is observed even with a substrate : catalyst ratio of 500 : 1. This shows that the reaction can proceed with a lesser amount of catalyst.

An additional activation of silicon atom by the fluoride anion is well known (see Ref. 20). Figure 7 illustrates the structure of a hypothetical intermediate state of the reaction that takes into account the experimental facts observed.

Thus, positively charged Co^{III} complexes, formed by Schiff monobases of salycylic aldehydes and chiral diamines (**1—3**), synthesized in our group, proved to be highly effective activators of the trimethylsilylcyanation reaction. They act as bifunctional chiral catalysts having both acidic and basic groups in a molecule. The effectiveness of the resulting complexes is on a level with the most active catalysts of this reaction known in literature. Compounds **1—3** are readily modified by a series of diamines and salycylic aldehydes. It can be expected that modest values of asymmetric inductions observed could be further improved, and the complexes **1—3** could be successively used as catalysts for other reactions involving C—C bond formation. Thus, the synthesis of chiral bifunctional catalysts of a fundamentally new class was successful. Accordingly, the problem of development of a novel class of chiral bifunctional catalysts formulated in the introduction was successfully solved.

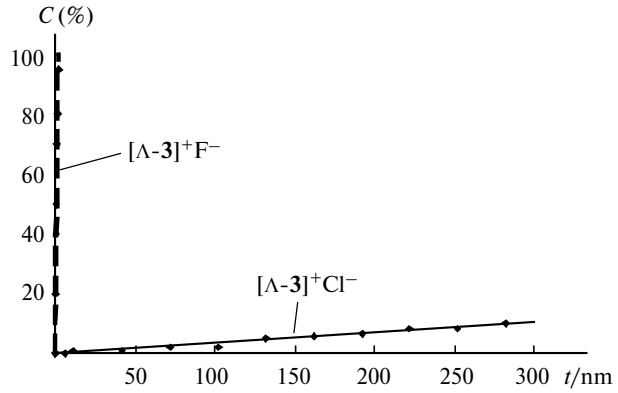


Fig. 6. Relative rate of *O*-trimethylsilylmandelonitrile formation in catalytic reaction between TMSCN and PhCHO with complexes $[\Lambda\text{-}\mathbf{3}]^+F^-$ and $[\Lambda\text{-}\mathbf{3}]^+Cl^-$ (0.5 мол.%) in CH_2Cl_2 at room temperature.

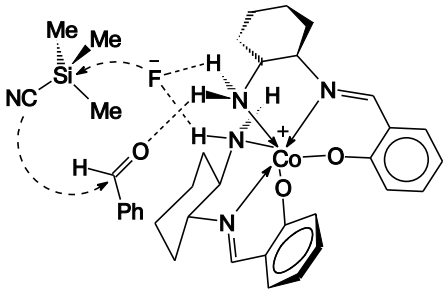


Fig. 7. Structure of a hypothetic transition state for the reaction of the trimethylsilylcyanation of benzaldehyde.

Experimental

NMR spectra were recorded on «Bruker Avance 300» instrument, working at resonance frequencies of 300.13 MHz (^1H) and 282.38 MHz (^{19}F), NOESY experiment was performed using a «Bruker Avance 600» instrument, working at resonance frequencies of 600.22 MHz (^1H) and 282.38 MHz (^{19}F). Proton chemical shifts (δ, ppm) were measured relative to the residual solvent peak of a non-deutered solvent. As solvents $CDCl_3$, CD_3OD, D_2O and $(CD_3)_2CO$ were used. Optical rotations were measured with a «Perkin—Elmer 341» polarimeter using a 5 cm thermostated cuvette at 25 °C. In the study, sorbents such as silica gel 60 («Merck») and Sephadex LH-20 («Supelco») were used.

Enantiomeric analysis of trimethylsilyl cyanohydrine ethers was performed on a gas chromatograph 3700, equipped with a plazma ionization detector, using a chiral stationaly phase DP-TFA-γ-cD (32 м×0.20 мм), with hydrogen as a carrier gas. A racemic form of each compound was used as a standard.

Elemental analysis for all the compounds obtained was performed in the Laboratory of Elemental Analysis of INEOS RAS. All the solvents in use were purified according to convenient procedures.

$Na_3[Co(CO_3)_3]$ was synthesized according to the previously reported procedure (see Ref. 21).

Synthesis of (1*R*,2*R*)-1,2-diaminocyclohexane. Resolution of the commercially available 1,2-*trans*-cyclohexanediamine («Aldrich») was performed according to the known procedure (see Ref. 22). Enantiomeric purity of the compound, determined for its bis-trifluoroacetyl derivative using chiral gas chromatography, exceeded 99%.

Synthesis of cationic complexes of the Co^{III} ion (general procedure)

Synthesis of the Schiff monobase derived from (1*R*,2*R*)-1,2-diaminocyclohexane and salycylic and substituted salycylic aldehydes. To the cooled on an ice bath solution of (1*R*,2*R*)-1,2-diaminocyclohexane (0.5 mL, 0.475 g, 4.16 mmol) in $CHCl_3$ (50 mL) a solution of salycylic (or substituted salycylic) aldehyde (2 mmol) in $CHCl_3$ (50 mL) was slowly added dropwise (over 3 h). Then the reaction mixture was stirred for 5 h without interrupting, and evaporated to dryness in vacuo. The resulting yellow oily substance, presenting a mixture of mono- and bis-Schiff bases in a ~6 : 1 ratio, was used further without any purification. The yield of the target mono Schiff base exceeded 80%.

Synthesis of chiral positively charged octahedral cobalt(III) complexes. To the Schiff base (2 mmol) dissolved in ethanol (12 mL), $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (0.4 g, 1.1 mmol) was added. The reaction mixture was refluxed for 3 h, then the undissolved residue of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ was filtered, and the filtrate was evaporated to dryness in vacuo. Λ-Isomer of complex was separated from the corresponding concomitant by-products and a minor amount of Δ-isomer by column chromatography (SiO_2, 2×10 cm, $CHCl_3/(CH_3)_2CO$ in a 5 : 1 ratio), with a preliminary change of the counterion by chlorine, since in this case the separation is more effective. The second dark-brown fraction from the column comprises the target Λ-isomer*. Then the complex with Cl^- counterion was purified by gel chromatography on «Sephadex LH-20», eluting with EtOH/C_6H_6 mixture in a 1 : 1 ratio. To change counterions, 0.16 mmol of the complex obtained was dissolved in 50% aqueous EtOH (10 mL) and passed through a column (20×100 mm) packed with anion-exchange resin that contains the required anion (F^-, BF_4^- or any other) as a counterion. Removal of the solvent in vacuo and drying in a dessicator over P_2O_5 gave the target product.

Catalytic trimethylsilylcyanation of benzaldehyde (general procedure). A solution of the catalyst (2.0 mol.%, 0.005 mmol) in CH_2Cl_2 (1 mL) was placed in a Schlenk flask under argon flow, followed by a consequtive addition of benzaldehyde (0.025 mL, 0.0261 g, 0.25 mmol) and trimethylsilyl cyanide (0.04 mL, 0.0317 g, 0.32 mmol). The reaction mixture was stirred under argon at 25 °C for a certain time, then the catalyst was removed by flash chromatography on SiO_2 (ø 2 mm×10 m, eluent — CH_2Cl_2). Enantiomeric excess of the product obtained was determined by the gas chromatography on a chiral column.

Λ-Bis[2-{[(1*R*,2*R*)-2-aminocyclohexyl]iminomethyl}phenolate]cobalt(III) chloride [Λ-1]$^+$Cl$^-$. Yield 278 mg (45%), $[\alpha]^{25}_D$ −1610 (*c* 0.056, MeOH). Found (%): C, 51.75; H, 5.80; Cl, 16.46; Co, 9.4; N, 8.9. $C_{26}H_{34}ClCoN_4O_2\cdot 0.6CHCl_3\cdot H_2O$. Calculated (%): C, 51.65; H, 5.96; N, 9.06; Cl, 16.05; Co, 9.53. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.17—1.36 (m, 1 H, —CH_2—); 1.53 (dd, 1 H, —CH_2—, *J* = 26.0 Hz, *J* = 12.9 Hz); 1.72—2.09 (m, 5 H, —CH_2—, —NH_2); 2.31 (dd, 1 H, —CH_2—, *J* = 22.0 Hz, *J* = 12.4 Hz); 2.63 (d, 1 H, —CH_2—, *J* = 11.0 Hz); 2.78 (d, 1 H, >CH—N, *J* = 9.3 Hz); 3.90 (br. t, 1 H, >CH—N, *J* = 9.9 Hz); 6.40—6.57 (m, 2 H, Ar,—NH_2); 6.63 (d, 1 H, Ar, *J* = 8.4 Hz); 7.04 (ddd, 1 H, Ar, *J* = 8.6 Hz, *J* = 7.0 Hz, *J* = 1.7 Hz); 7.23 (dd, 1 H, Ar, *J* = 7.80 Hz, *J* = 1.60 Hz); 7.97 (s, 1 H, —CH=N).

Λ-Bis[2-{[(1*R*,2*R*)-2-aminocyclohexyl]iminomethyl}phenolate]cobalt(III) fluoride [Λ-1]$^+$F$^-$. Yield 245 mg (40%), $[\alpha]^{25}_D$ −1850 (*c* 0.076, MeOH). Found (%): C, 52.38; H, 5.98; F, 2.34; Co, 9.4; N, 8.92. $C_{26}H_{34}FCoN_4O_2\cdot 0.7CHCl_3\cdot H_2O$. Calculated (%): C, 52.22; H, 6.02; N, 9.12; F, 3.09; Co, 9.6. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.11 (m, 1 H, —CH_2—); 1.15—2.06 (m, 8 H, —CH_2—, —NH_2); 2.70 (d, 1 H, >CH—N, *J* = 10.2 Hz); 2.90 (s, 1 H, —NH_2); 3.55 (dd, 1 H, >CH—N, *J* = 14.1 Hz, *J* = 7.1 Hz); 6.61 (t, 1 H, Ar, *J* = 7.3 Hz); 6.96 (d, 1 H, Ar, *J* = 8.4 Hz); 7.16 (t, 1 H, Ar, *J* = 7.3 Hz); 7.22 (d, 1 H, Ar, *J* = 7.8 Hz); 7.88 (s, 1 H, —CH=N). ^{19}F NMR ($CDCl_3$), δ: −72.405.

Λ-Bis[2-{((1*R*,2*R*)-2-aminocyclohexyl)iminomethyl}phenolate]cobalt(III) tetrafluoroboride [Λ-1]$^+$BF$_4^-$. Yield 244 mg (42%). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.25 (m, 1 H, —CH_2—); 1.49 (d, 1 H, —CH_2—, *J* = 12.7 Hz); 1.72—2.10 (m, 5 H, —CH_2—, —NH_2); 2.33 (m, 1 H, —CH_2—), 2.55—2.72 (m, 1 H, —CH_2—); 2.78 (d, 1 H, >CH—N, *J* = 8.9 Hz); 3.89 (br. t, 1 H, >CH—N, *J* = 9.4 Hz); 6.52 (m, 2 H, Ar, —NH_2); 6.64 (d, 1 H, Ar, *J* = 8.4 Hz); 6.99—7.11 (m, 1 H, Ar); 7.23 (dd, 1 H, Ar, *J* = 7.9 Hz, *J* = 1.7 Hz); 7.98 (s, 1 H, —CH=N—). ^{19}F NMR ($CDCl_3$), δ: −69.91.

Λ-Bis[2-methoxy-6-{[(1*R*,2*R*)-2-aminocyclohexyl]iminomethyl}phenolate]cobalt(III) chloride [Λ-2]$^+$Cl$^-$. Yield 253 mg (43%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ: 1.18—1.56 (m, 3 H, —CH_2—); 1.61—1.98 (m, 4 H, —CH_2—); 2.22—2.40 (m, 1 H, —CH_2—); 2.70 (dd, 1 H, >CH—N, *J* = 11.0 Hz); 3.28 (s, 3 H, OCH_3); 3.33 (br. s, 1 H, —NH_2); 3.94 (br. t, 1 H, >CH—N, *J* = 10.8 Hz); 6.30 (t, 1 H, Ar, *J* = 7.7 Hz); 6.63 (dd, 1 H, Ar, *J* = 7.7, *J* = 1.6 Hz); 6.75 (br. t, 1 H, —NH_2, *J* = 9.4 Hz); 7.06 (dd, 1 H, —CH=N—, *J* = 7.9 Hz, *J* = 1.6 Hz).

Λ-Bis[2-allyl-6-{[(1*R*,2*R*)-2-aminocyclohexyl]iminomethyl}phenolate]cobalt(III) chloride [Λ-3]$^+$Cl$^-$. Yield 317 mg (47%). M.p. 160—162 °C, $[\alpha]^{25}_D$ −2470 (*c* 0.06, MeOH). Found (%): C, 57.66; H, 6.56; Cl, 11.44; N, 7.89. $C_{32}H_{42}ClCoN_4O_2\cdot 0.4CHCl_3\cdot H_2O$. Calculated (%): C, 57.66; H, 6.63; N, 8.3; Cl, 11.56. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.16—1.34 (m, 1 H, —CH_2—); 1.45—2.12 (m, 6 H, —CH_2—, —NH_2); 2.35 (dt, 1 H, —CH_2—, *J* = 21.9 Hz, *J* = 11.0 Hz); 2.51—2.72 (m, 1 H, —CH_2—); 2.72—2.95 (m, 3 H, >CH—N, —CH_2— (All)); 3.92 (t, 1 H, >CH—N, *J* = 9.6 Hz); 4.69 (dd, 13.5, 2 H, =CH_2 (All), *J* = 20.9 Hz); 5.34 (m, 1 H, =CH— (All)); 6.39—6.66 (m, 2 H, Ar, —NH_2); 6.92 (d, 1 H, Ar, *J* = 7.0 Hz); 7.05—7.19 (m, 1 H, Ar); 7.96 (s, 1 H, —CH=N).

Λ-Bis[2-allyl-6-{[(1*R*,2*R*)-2-aminocyclohexyl]iminomethyl}phenolate]cobalt(III) fluoride [Λ-3]$^+$F$^-$. Yield 267 mg (42%), $[\alpha]^{25}_D$ −2621.1 (*c* 0.038, MeOH). Found (%): C, 60.72; H, 7.03; F, 2.34; N, 8.59. $C_{32}H_{42}FCoN_4O_2\cdot 0.2CHCl_3\cdot H_2O$. Calculated (%): C, 60.95; H, 7.02; F, 2.99; N, 8.83. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.20 (m, 2 H, —CH_2—); 1.38—2.19 (m, 7 H, —CH_2—, —NH_2); 2.53 (s, 1 H, —NH_2); 2.67—2.97 (m, 3 H, >CH—N, —CH_2— (All)); 3.66 (m, 1 H, >CH—N); 4.68 (dd, 2 H, =CH_2— (All), *J* = 23.6 Hz, *J* = 13.5 Hz); 5.23—5.47 (m, 1 H, =CH— (All)); 6.42 (t, 1 H, Ar, *J* = 7.4 Hz); 6.89 (d, 1 H, Ar, *J* = 6.8 Hz); 7.08 (d, 1 H, Ar, *J* = 7.5 Hz); 7.93 (s, 1 H, —CH=N).

Λ-Bis[2-allyl-6-{[(1*R*,2*R*)-2-aminocyclohexyl]iminomethyl}phenolate]cobalt(III) tetrafluoroboride [Λ-3]$^+$BF$_4^-$. Yield 270 mg (41%), $[\alpha]^{25}_D$ −2321.2 (*c* 0.066, MeOH). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.21 (m, 1 H, —CH_2—); 1.48 (dd, 1 H, —CH_2—, *J* = 25.5 Hz, *J* = 12.7 Hz); 1.59—2.07 (m, 5 H, —CH_2—, —NH_2); 2.27 (dd, 1 H, —CH_2—, *J* = 22.4 Hz, *J* = 12.0 Hz); 2.57 (d, 1 H, —CH_2—, *J* = 9.9 Hz); 2.68—2.91 (m, 3 H, >CH—N, —CH_2— (All)); 3.86 (br. t, 1 H, >CH—N, *J* = 9.4 Hz); 4.63 (m, 2 H, =CH_2— (All)); 5.19—5.40 (m, 1 H, =CH— (All)); 6.24—6.49 (m, 2 H, Ar, —NH_2); 6.85 (d, 1 H, Ar, *J* = 6.9 Hz); 7.07 (d, 1 H, Ar, *J* = 6.8 Hz); 7.92 (s, 1 H, —CH=N—). ^{19}F NMR ($CDCl_3$), δ: −69.842.

X-ray diffraction analysis of complexes [Λ-1]$^+$F$^-$ and [Λ-3]$^+$Cl$^-$. Unit cell parameters and reflexion intensities for the compounds [Λ-**1**]$^+$F$^-$ and [Λ-**3**]$^+$Cl$^-$ were measured with an automatic diffractometer «Bruker SMART APEX II CCD» (*T* = 100 K, Mo-Kα-radiation, graphite monochromator, φ- и ω-scanning). For the data obtained, the calculation of X-ray absorbance was performed using a computer programme SADABS[23]. Main crystal structural data are presented in Table 3.

* Minor Δ-isomer remains on the start and is not eluted by the system; and the first fraction (yellow one) is an unreacted Schiff base.

Table 3. Main crystallographic data and refining parameters for the compounds $[\Lambda\text{-}\mathbf{1}]^+F^-$ and $[\Lambda\text{-}\mathbf{3}]^+Cl^-$

Parameter	$[\Lambda\text{-}\mathbf{1}]^+F^- \cdot 2CHCl_3$	$[\Lambda\text{-}\mathbf{3}]^+Cl^- \cdot 0.25CH_3OH$
Empirical formula	$C_{28}H_{36}N_4O_2FCl_6Co$	$C_{32.25}H_{43}N_4O_{2.25}ClCo$
Molecular weight	751.24	617.09
T/K	100	100
Syngony	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a/Å	12.8489(14)	12.4079(8)
b/Å	8.4379(9)	20.2137(13)
c/Å	15.4329(16)	13.0439(8)
α/deg	90	90
β/deg	91.263(2)	108.829(1)
γ/deg	90	90
V/Å^3	1672.8(3)	3096.5(3)
Z	2	4
d_c/g cm^3	1.491	1.324
F(000)	772	1306
μ/mm^{-1}	1.030	0.677
$2\theta_{max}$/deg	55.6	52
Number of reflexions measured	18273	29676
Number of independent reflections	7862	12186
Number of reflections with $I > 2\sigma(I)$	7143	8550
Number of refined parameters	379	734
R_1 ($I > 2\sigma(I)$)	0.0627	0.0551
wR_2 (all data)	0.1596	0.1196
GOOF	1.003	1.003
Flack parameter	0.00(2)	0.02(2)
T_{min}/T_{max}	0.747/0.820	0.849/0.977

Structures of both compounds were determined by a direct method and refined by full-matrix least squares, with anisotropic displacement parameters for the non-hydrogen atoms. Single crystal of the compound $[\Lambda\text{-}\mathbf{1}]^+F^-$ comprises two solvate chloroform molecules in the independent part of the elemental cell, one of which is disordered in two positions with the occupancies 0.65:0.35. The independent part of the unit cell of the compound $[\Lambda\text{-}\mathbf{3}]^+Cl^-$ contains 1/2 of the solvate methanol molecule. Hydrogen atoms of amino groups and the solvate methanol molecule were detected objectively in the substractive Fourie-synthesis and included in a refinement with fixed positional (model «Rider») and thermal ($U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3-groups, $U_{iso}(H) = 1.5U_{eq}(O)$ for OH-group and $U_{iso}(H) = 1.2U_{eq}(N)$ for NH_2-groups) parameters. Positions of the other hydrogen atoms were calculated geometrically and refined in the isotropic approximation with fixed positional (model «Rider») and thermal ($U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3-groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for all the other groups) parameters. All calculations were performed using the complex of programmes SHELXTL (see Ref. 24).

Tables of atomic coordinates, bond lengths and anisotropic temperature parameters for the compounds $[\Lambda\text{-}\mathbf{1}]^+F^- \cdot 2CHCl_3$ and $[\Lambda\text{-}\mathbf{3}]^+Cl^- \cdot 1/4CH_3OH$ have been deposited with the Cambridge Crystallographic Data Centre (CCDC 889589 и 820740, correspondingly).

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