Lithium salts of chiral metallocomplex anions as catalysts for asymmetric trimethylsilylcyanation of aldehydes

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A series of the anionic Co^{III} complexes based on optically active amino acids containing the lithium cation in the external sphere of the complex was synthesized. The synthesized compounds were used as catalysts in the asymmetric addition of trimethylsilyl cyanide to aldehydes. The influence of the temperature, catalyst concentration, and modification of the chiral anion structure on the enantioselectivity of catalysis was studied.

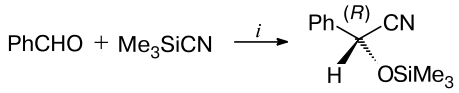
Key words: asymmetric trimethylsilylcyanation, chiral anions, lithium cation, Lewis acid, cyanohydrins.

In vast majority of the cases, metal complexes with chirality in the cationic part are used in asymmetric catalysis.[1] An alternative strategy, which involved the compounds bearing the chiral anion responsible for stereodifferentiation as catalysts, is very rare.[2] A specific feature of these catalytic systems is that the negative charge is delocalized inside rather bulky fragment and, hence, the charge of the outer-sphere cation is compensated to a less extent. Therefore, the cation is a stronger Lewis acid than the same ion chelated by chiral ligands. Thus, even alkali metal cations can be "transformed" into efficient Lewis acids. Only several examples of asymmetric reactions catalyzed by the ion pairs [alkali metal cation]$^+$ [chiral anion]$^-$ were described.[3—7] A family of heterobimetallic catalysts representing rare-earth metal complexes with chiral binaphthol and alkali metal cations in the outer sphere of the complex has previously[3] been synthesized. They were used in the aldol reaction and the Michael asymmetric addition. Binaphthol monolithium salt was used in the asymmetric trimethylsilylcyanation of aldehydes.[4] The influence of water additives on the enantioselectivity of this reaction was studied.[5] The cyanosilylation of ketones in the presence of lithium salts of phosphoric acids based on binaphthol was studied.[6] 3,3´-Dichlorobinaphthol dilithium salt was used in the asymmetric aldol reaction.[7]

It is considered that among alkali metals the lithium cation possesses the highest Lewis acidity.[8] It was shown[9] that a solution of lithium salt of permethylated icosahedral monocarbadodecaborate $LiCB_{11}Me_{12}$ in benzene is an efficient catalyst for pericyclic reactions. It seems practically important to use $LiCB_{11}Me_{12}$ as a catalyst of alkene radical polymerization.[10]

In the previous work,[11] we used the chiral anionic complexes of Λ- and Δ-bis[*N*-salicylidene-(*S*)-aminoacidato]-cobaltates[12] with potassium, sodium, and silver cations as Lewis acids in the asymmetric trimethylsilylcyanation of aldehydes and in the Mukayama reaction. We assumed that the rate of benzaldehyde trimethylsilylcyanation should increase with stronger Lewis acids, *viz.*, complexes containing the lithium ion in the outer sphere. Indeed, it turned out that the half-conversion time of the addition of trimethylsilyl cyanide (TMSCN) to benzaldehyde (Scheme 1) catalyzed by the complex $Li^+[\Delta\text{-}\mathbf{1}]^-$ (the structure of the complex is shown in Scheme 2) is 1.3 min and the enantioselectivity reaches 23%, whereas for the complexes $Na^+[\Delta\text{-}\mathbf{1}]^-$ and $K^+[\Delta\text{-}\mathbf{1}]^-$ the half-conversion period is 5 and 6 min, respectively, and the product is formed as a racemate in the both cases.

Scheme 1



i. Catalyst (2 mol.%), CH_2Cl_2, argon, 1 h, 25 °C.

In the present work, we studied the catalytic activity and stereodifferentiating ability of lithium salts of Λ- and Δ-bis[*N*-salicylidene-(*S*)-aminoacidato]cobaltates in the trimethylsilylcyanation of aldehydes.

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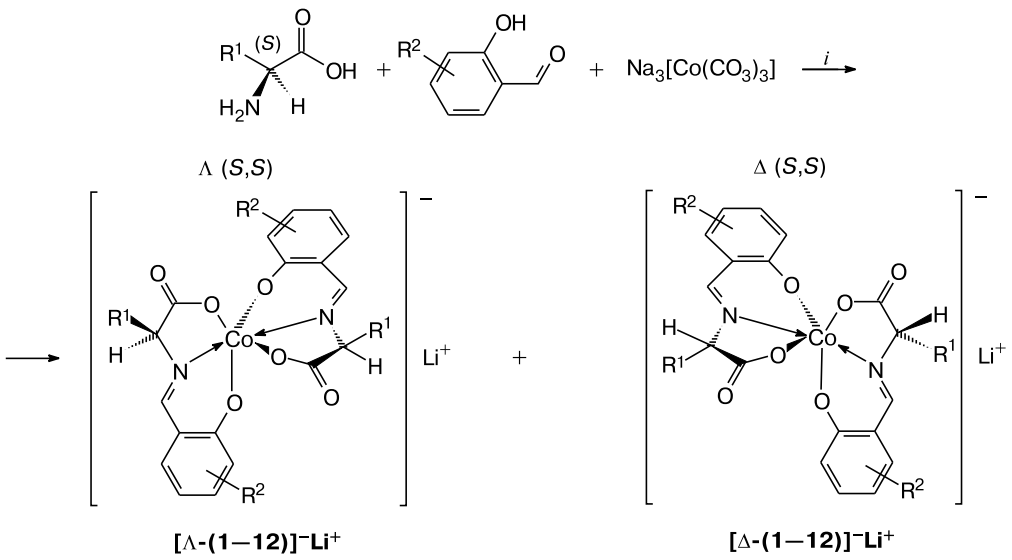
Results and Discussion

Bis[*N*-salicylidene-(*S*)-aminoacidato]cobaltate anions are coordinately saturated cobalt(III) complexes with two perpendicular tridentate ligands, Schiff bases of salicylaldehyde and (*S*)-amino acids. They exist as meridional Λ- and Δ-diastereomers, which do not transform into each other under normal conditions, *i.e.*, they are stereochemically inert.[13] The complexes were synthesized by the reaction of $Na_3[Co(CO_3)_3]$ with the corresponding amino acid and salicylaldehyde or substituted salicylaldehyde in ethanol (modified procedure,[14] see Scheme 2) followed by the chromatographic separation of diastereomers and were used further for catalysis. As a rule, the synthesis yielded an excess of Δ-(*S,S*)-diastereomer[13] with a lower R_f value compared to that of the Λ-(*S,S*)-isomer obtained by the chromatographic separation on alumina.[12] Then the complexes containing the lithium ion as a counterion were obtained by ion-exchange chromatography. The complexes based on (*S*)-valine, (*S*)-*tert*-leucine, (*S*)-threonine, (*S*)-tryptophane, and (*S*)-phenylalanine were synthesized according to the presented procedure, because it was interesting to reveal the dependence of the catalytic activity and stereodifferentiating ability of the complexes on the volume of the amino acid radical and the influence of the functional groups in the side chain of the amino acid on the enantioselectivity of catalysis.

The presence of substituents in the salicylidene fragment possibly favors the additional binding of the lithium cation and/or the change in its localization on the chiral metallocomplex anion. Therefore, to synthesize the complexes, we used along with salicylaldehyde its substituted analogs: 3-allyl-5-bromo-, 3-allyl-, 3,5-dichloro-, 3-methoxy-, and 3-phenylsalicylaldehydes. It should be mentioned that, in the case of complex **2**, the reaction afforded a mixture of diastereomers with such a considerable predomination of the Δ-isomer that it was impossible to isolate any amount of the Λ-isomer in the pure state. The assignment of the complexes to the Λ- or Δ-series has been described earlier.[13]

The catalytic activity of the synthesized complexes was studied in the model reaction of benzaldehyde trimethyl-

Scheme 2



Complex	R^1	R^2	Λ : Δ*	Complex	R^1	R^2	Λ : Δ	Complex	R^1	R^2	Λ : Δ
1	Pr^i	H	1 : 7	**5**	CH(OH)Me	3,3′-Allyl-5,5′-Br	1 : 7	**9**	CH_2Ind	3,3′-OMe	2 : 7
2	CH(OH)Me	H	**	**6**	CH_2Ind	3,3′-Allyl-5,5′-Br	1 : 3	**10**	Bu^t	3,3′-OMe	1 : 1
3	CH_2Ph	H	1 : 6	**7**	Pr^i	3,3′,5,5′-Cl	1 : 3	**11**	Pr^i	3,3′-Allyl	2 : 7
4	Pr^i	3,3′-Allyl-5,5′-Br	1 : 2	**8**	Pr^i	3,3′-OMe	1 : 3	**12**	Pr^i	3,3′-Ph	5 : 8

* Ratio of the Λ- and Δ-isomers.
** Only the Δ-isomer was isolated.

Reagents and conditions: *i*. (1) EtOH, reflux, 3 h; (2) chromatographic separation on Al_2O_3 (EtOH); (3) ion-exchange chromatography and additional purification by gel chromatography on Sephadex LH-20 (C_6H_6—EtOH, 3 : 1).

silylcyanation (see Scheme 1). The reaction was carried out in dichloromethane under argon atmosphere at room temperature for 1 h. All the synthesized complexes demonstrated very high catalytic activity, providing the formation of (*R*)-*O*-trimethylsilylmandelonitrile in a yield higher than 98%, whereas the reaction does not occur without a catalyst. The enantiomeric excess values of (*R*)-*O*-trimethylsilylmandelonitrile obtained by using various complexes as catalysts are listed in Table 1.

It is interesting that in the absence of substituents in the salicylaldehyde fragment the stereodifferentiating ability of the Λ- and Δ-complexes is indiscernible (see Table 1, entries *1* and *13*). The stereodifferentiating ability of the complexes with different configurations becomes different upon the introduction of substituents into the salicylidene fragment (see Table 1, entries *8* and *19*). An increase in the radical bulkiness in the amino acid moiety of the complexes results in the formation of trimethylsilylmandelonitrile with an opposite configuration (see Table 1, entry *21*). The complexes containing the hydroxyl or indolyl group in the amino acid moiety catalyzed racemic product formation (see Table 1, entries *2*, *9*, and *20*). The complex with the Λ-configuration bearing allyl groups in the salicylidene fragments $Li^+[\Lambda\text{-}\mathbf{11}]^-$ have the highest stereodifferentiation. In this case, the enantioselectivity of the reaction was 50% (see Table 1, entry *22*). A decrease in the reaction temperature to −20 °C made it possible to increase the product *ee* up to 60% (see Table 1, entry *22*). Thus, we found that the enantioselectivity of benzaldehyde trimethylsilylcyanation depends on both the nature of substituents in the amino acid and salicylidene moieties and stereochemistry of the complex.

It was also interesting to study the influence of the catalyst concentration on the rate and enantioselectivity of benzaldehyde trimethylsilylcyanation. The plots of the yield and enantiomeric excess of trimethylsilylmandelonitrile *vs* concentration of the $Li^+[\Lambda\text{-}\mathbf{8}]^-$ catalyst are shown in Fig. 1. It turned out that the $Li^+[\Lambda\text{-}\mathbf{8}]^-$ complex does not lose activity even at the substrate to catalyst ration equal to 1000 : 1. However, in this case, the enantiomeric excess of the reaction product decreases to 19%. The enantioselectivity curve reaches a plateau with an increase in the catalyst concentration. It seems that the catalytically active species responsible for the asymmetric induction involve several molecules of complexes and their amounts depend on the concentration of the catalyst. Interestingly, without a solvent the trimethylsilylcyanation reaction catalyzed by the $Li^+[\Lambda\text{-}\mathbf{8}]^-$ complex occurs also rather effi-

Table 1. Asymmetric addition of TMSCN to PhCHO[a]

Entry	Catalyst	*ee* (%) (configuration)[b]
1	$Li^+[\Delta\text{-}\mathbf{1}]^-$	23(*R*)
2	$Li^+[\Delta\text{-}\mathbf{2}]^-$	0
3	$Li^+[\Delta\text{-}\mathbf{3}]^-$	0
4	$Li^+[\Delta\text{-}\mathbf{4}]^-$	4(*R*)
5	$Li^+[\Delta\text{-}\mathbf{5}]^-$	22(*R*)
6	$Li^+[\Delta\text{-}\mathbf{6}]^-$	10(*R*)
7	$Li^+[\Delta\text{-}\mathbf{7}]^-$	33(*R*)
8	$Li^+[\Delta\text{-}\mathbf{8}]^-$	24(*R*)
9	$Li^+[\Delta\text{-}\mathbf{9}]^-$	6(*R*)
10	$Li^+[\Delta\text{-}\mathbf{10}]^-$	0
11	$Li^+[\Delta\text{-}\mathbf{11}]^-$	0
12	$Li^+[\Delta\text{-}\mathbf{12}]^-$	7(*R*)
13	$Li^+[\Lambda\text{-}\mathbf{1}]^-$	22(*R*)
14	$Li^+[\Lambda\text{-}\mathbf{3}]^-$	22(*R*)
15	$Li^+[\Lambda\text{-}\mathbf{4}]^-$	40(*R*)
16	$Li^+[\Lambda\text{-}\mathbf{5}]^-$	10(*R*)
17	$Li^+[\Lambda\text{-}\mathbf{6}]^-$	6(*R*)
18	$Li^+[\Lambda\text{-}\mathbf{7}]^-$	7(*R*)
19	$Li^+[\Lambda\text{-}\mathbf{8}]^-$	40(*R*)/36(*R*)[c]
20	$Li^+[\Lambda\text{-}\mathbf{9}]^-$	0
21	$Li^+[\Lambda\text{-}\mathbf{10}]^-$	12(*S*)
22	$Li^+[\Lambda\text{-}\mathbf{11}]^-$	50(*R*)/60(*R*)[d]
23	$Li^+[\Lambda\text{-}\mathbf{12}]^-$	20(*R*)

[a] Reaction conditions: PhCHO (1 mmol), TMSCN (1.1 mmol), catalyst (0.02 mmol), CH_2Cl_2 (1 mL), 25 °C, argon, 1 h. The yield of the product was >95% in all cases.
[b] Determined by GLC on the chiral phase.
[c] The reaction was carried out without a solvent.
[d] The reaction was carried out at −20 °C for 24 h.

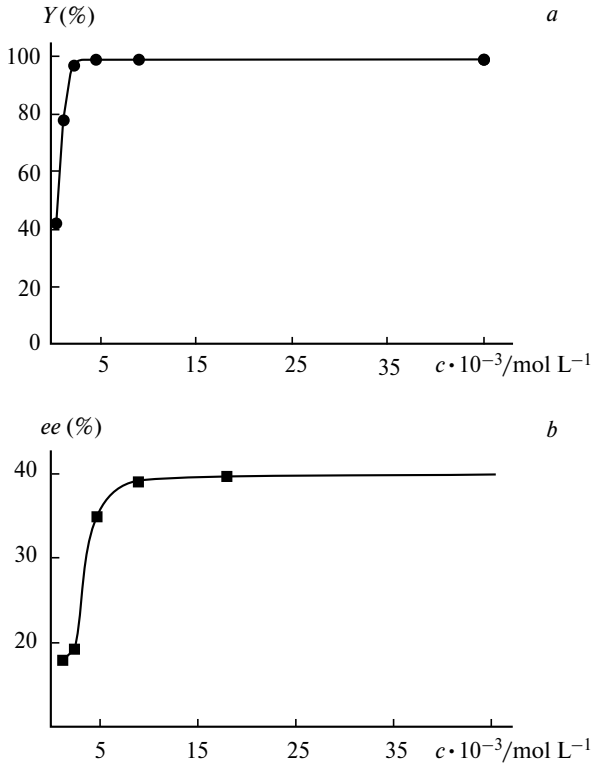


Fig. 1. Dependences of the yield (*Y*) (*a*) and enantiomeric excess (*ee*) (*b*) of trimethylsilylmandelonitrile on the concentration of the $Li^+[\Lambda\text{-}\mathbf{8}]^-$ catalyst.

Table 2. Asymmetric addition of TMSCN to aldehydes[a]

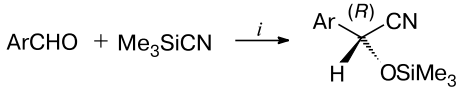
Entry	Aldehyde	Yield (%)	*ee* (%)[b,c]
1	4-FC_6H_4CHO	>90	32
2	2-ClC_6H_4CHO	>90	42
3	PhCH=CHCHO	>90	37

[a] Reaction conditions: aldehyde (1 mmol), TMSCN (1.1 mmol), catalyst (0.02 mmol), CH_2Cl_2 (1 mL), argon, −20 °C, 24 h.
[b] Determined by GLC on the chiral phase.
[c] The products with the (*R*)-configuration were isolated.

ciently to form the product with an enantiomeric excess of 36% (see Table 1, entry *19*).

To extend the substrate scope, we tested TMSCN addition to other aldehydes (Scheme 3, Table 2) and acetophenone using the $Li^+[\Lambda$-**11**$]^-$ complex with the highest stereodifferentiating ability.

Scheme 3



i. Catalyst (2 mol.%), CH_2Cl_2, argon, 24 h, −20 °C.

In the case of aldehydes, the quantitative yield of the product was observed if the reaction was carried out at −20 °C for 1 day. Under the same conditions, the reaction with acetophenone occurred in a yield of 53% and an enantioselectivity of 27%. The introduction of electron-withdrawing substituents into the benzaldehyde molecule insignificantly decreases the enantioselectivity of the process (see Table 2, entries *1* and *2*). When cinnamic aldehyde was used, the enantiomeric excess of the product was lower than that in the case of benzaldehyde (see Table 2, entry *3*).

Thus, the strategy described in this work demonstrates the possibility of using the chiral metallocomplex anions with lithium cations in the outer sphere as catalysts for the asymmetric addition of trimethylsilyl cyanide to aldehydes and ketones. The properties of the catalytic systems can be varied due to the simple synthesis and structural modification of the metallocomplex anions.

Experimental

^{1}H NMR spectra were recorded on Bruker Avance-300 (300 MHz) and Bruker Avance-400 (400 MHz) spectrometers. Chemical shifts were measured in the δ scale relative to the signal of residual protons of the deuterated solvent. Optical rotation was measured on a Perkin—Elmer 341 polarimeter in a temperature-maintained cell (l = 5 cm) at 25 °C. The solvent and concentration in grams per 100 mL of the solvent are indicated for all compounds. Elemental analyses of all synthesized compounds were performed at the Laboratory of Elemental Analysis of the A. N. Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences). Silica gel Kieselgel 60 (Merck), Al_2O_3 (Chemapol), and Sephadex LH-20 (Supelco) were used. Solvents were purified according to standard procedures. Freshly distilled aldehydes and TMSCN were used. Enantiomeric analysis of the synthesized trimethylsilylated cyanohydrin was carried out on a gas chromatograph (Perkin Elmer sigma 2000 model) equipped with a flame-ionization detector on the Chiraldex B·DM stationary phase (30 m×0.25 mm). The racemic form was used as a standard for each compound. Sodium tricarbonatocobaltate(III) $Na_3[Co(CO_3)_3]$ was synthesized by the described procedure[15] as a dark green powder, m.p. >300 °C.

Synthesis of lithium bis[*N*-salicylideneaminoacidato]cobaltate* 1—12 (general procedure). Salicylaldehyde (or substituted salicylaldehyde) (10 mmol) was added with stirring to a mixture of $Na_3[Co(CO_3)_3\cdot 3H_2O]$ (5 mmol) and (*S*)-amino acid (10 mmol) in EtOH (25 mL). The reaction mixture was refluxed for 3 h, and the precipitate was filtered off. The solvent was removed *in vacuo*, and the residue was washed with diethyl ether and dissolved in EtOH. The isomers were separated by column chromatography (Al_2O_3, EtOH as eluent). The Λ- or Δ-isomers were additionally purified by gel chromatography on Sephadex LH-20 (EtOH—benzene (1 : 3) mixture as eluent). To obtain the lithium salts, the prepared complex (0.1 mmol) was dissolved in 50% aqueous EtOH (10 mL) and passed through a column (100×20 mm) with the ion-exchange resin DOWEX-50w×8 containing Li^+ ions as counterions. The solvent was removed *in vacuo*, and the substance was additionally purified by gel chromatography on Sephadex LH-20 using an EtOH—benzene (1 : 3) mixture as eluent.

Lithium Λ-bis[*N*-salicylidene-(*S*)-valinato]cobaltate (Li^+[Λ-1]$^-$). The yield was 11%, $[\alpha]_D^{25}$ −4030 (*c* 0.032, MeOH). Found (%): C, 53.15; H, 5.66; N, 5.11. $C_{24}H_{26}N_2O_6CoLi\cdot 2H_2O$. Calculated (%): C, 53.34; H, 5.60; N, 5.18. ^{1}H NMR (400 MHz, D_2O), δ: 1.1 (dd, 12 H, CH_3-Val, J = 6.6 Hz, J = 3.7 Hz); 2.37—2.42 (m, 2 H, β-H-Val); 4.48 (d, 2 H, α-H-Val, J = 7.2 Hz); 6.38 (d, 2 H, Ar, J = 8.4 Hz); 6.62 (d, 2 H, Ar, J = 7.4 Hz); 6.95 (ddd, 2 H, Ar, J = 8.7 Hz, J = 7.2 Hz, J = 1.7 Hz); 7.45 (dd, 2 H, Ar, J = 7.8 Hz, J = 1.6 Hz); 8.4 (s, 2 H, CH=N).

Lithium Δ-bis[*N*-salicylidene-(*S*)-valinato]cobaltate (Li^+[Δ-1]$^-$). The yield was 74%, $[\alpha]_D^{25}$ −8630 (*c* 0.032, MeOH). Found (%): C, 53.11; H, 5.72; N, 5.09. $C_{24}H_{26}N_2O_6CoLi\cdot 2H_2O$. Calculated (%): C, 53.34; H, 5.60; N, 5.18. ^{1}H NMR (400 MHz, D_2O), δ: 1.07 (d, 6 H, CH_3-Val, J = 6.8 Hz); 1.17 (d, 6 H, CH_3-Val, J = 6.8 Hz); 2.47—2.52 (m, 2 H, β-H-Val); 4.37 (d, 2 H, α-H-Val, J = 6.4 Hz); 6.68 (t, 2 H, Ar, J = 6.9 Hz); 6.79 (d, 2 H, Ar, J = 8.4 Hz); 7.17 (ddd, 2 H, Ar, J = 8.6 Hz, J = 7.1 Hz, J = 1.7 Hz); 7.5 (dd, 2 H, Ar, J = 7.8 Hz, J = 1.7 Hz); 8.44 (s, 2 H, CH=N).

Lithium Δ-bis[*N*-salicylidene-(*S*)-threoninato]cobaltate (Li^+[Δ-2]$^-$). The yield was 70%, $[\alpha]_D^{25}$ −5720 (*c* 0.031, MeOH). Found (%): C, 48.61; H, 4.70; N, 5.23. $C_{22}H_{22}N_2O_8CoLi\cdot 2H_2O$. Calculated (%): C, 48.54; H, 4.81; N, 5.15. ^{1}H NMR (300 MHz, D_2O), δ: 1.3 (d, 6 H, CH_3-Thr, J = 8.6 Hz); 4.18—4.22 (m, 2 H, β-H-Thr); 4.5 (d, 2 H, α-H-Thr, J = 8.4 Hz); 6.6 (m, 4 H, Ar); 7.2 (t, 2 H, Ar, J = 9.6 Hz); 7.5 (d, 2 H, Ar, J = 9.8 Hz); 8.6 (s, 2H, CH=N).

* All complexes described in the present work melt at the temperature above 300 °C.

Lithium Λ-bis[*N*-salicylidene-(*S*)-phenylalaninato]cobaltate ($Li^+[Λ\text{-}3]^-$). The yield was 11%, $[\alpha]_D^{25}$ −3950 (*c* 0.032, MeOH). Found (%): C, 62.05; H, 4.53; N, 4.41. $C_{32}H_{26}N_2O_6CoLi \cdot H_2O$. Calculated (%): C, 62.15; H, 4.56; N, 4.53. ^{1}H NMR (300 MHz, D_2O), δ: 3.26, 3.55 (both AB part of ABX system, 4 H, CH_2-Phe, J_{AB} = 13.7 Hz, J_{AX} = 11.3 Hz, J_{BX} = 3.6 Hz); 5.05 (X part of ABX system, 2 H, α-H-Phe); 6.62 (d, 2 H, Ar, *J* = 8.5 Hz); 6.51 (t, 2 H, Ar, *J* = 8.5 Hz); 6.89 (ddd, 2 H, Ar, *J* = 8.5 Hz, *J* = 7.5 Hz, *J* = 1 Hz); 7.0 (d, 2 H, Ar, *J* = 7.5 Hz); 7.24 (s, 2 H, CH=N); 7.38 (m, 10 H, Ph).

Lithium Δ-bis[*N*-salicylidene-(*S*)-phenylalaninato]cobaltate ($Li^+[Δ\text{-}3]^-$). The yield was 66%, $[\alpha]_D^{25}$ −4600 (*c* 0.030, MeOH). Found (%): C, 62.21; H, 4.44; N, 4.56. $C_{32}H_{26}N_2O_6CoLi \cdot H_2O$. Calculated (%): C, 62.15; H, 4.56; N, 4.53. ^{1}H NMR (300 MHz, D_2O), δ: 3.32, 3.6 (both AB part of ABX system, 4 H, CH_2-Phe, J_{AB} = 13.8 Hz, J_{AX} = 9.5 Hz, J_{BX} = 3.7 Hz); 5.00 (X part of ABX system, 2 H, α-H Phe); 6.57 (d, 2 H, Ar, *J* = 9.3 Hz); 6.62 (t, 2 H, Ar, *J* = 9.3 Hz); 6.82 (m, 2 H, Ar); 7.07 (d, 2 H, Ar, *J* = 9.3 Hz); 7.11 (s, 2 H, CH=N); 7.40 (m, 10 H, Ph).

Lithium Λ-bis[*N*-(3-allyl-5-bromosalicylidene)-(*S*)-valinato]cobaltate ($Li^+[Λ\text{-}4]^-$). The yield was 30%, $[\alpha]_D^{25}$ −3560 (*c* 0.035, MeOH). Found (%): C, 46.53; H, 4.64; N, 3.76. $C_{30}H_{32}N_2O_6Br_2CoLi \cdot 2\,H_2O$. Calculated (%): C, 46.30; H, 4.66; N, 3.60. ^{1}H NMR (300 MHz, CD_3OD), δ: 1.2 (d, 6 H, CH_3-Val, *J* = 2.1 Hz); 1.23 (d, 6 H, CH_3-Val, *J* = 2.1 Hz); 2.47—2.60 (m, 2 H, β-H-Val); 2.69—2.75 (m, 4 H, CH_2 of allyl); 4.40 (d, 2 H, α-H-Val, *J* = 7.2 Hz); 4.78 (m, 4 H, =CH_2 of allyl); 5.28—5.34 (m, 2 H, =CH of allyl); 6.81 (d, 2 H, Ar, *J* = 2.7 Hz); 7.39 (d, 2 H, Ar, *J* = 2.7 Hz); 8.35 (s, 2 H, CH=N).

Lithium Δ-bis[*N*-(3-allyl-5-bromosalicylidene)-(*S*)-valinato]cobaltate ($Li^+[Δ\text{-}4]^-$). The yield was 53%, $[\alpha]_D^{25}$ −4890 (*c* 0.030, MeOH). Found (%): C, 46.38; H, 4.84; N, 3.62. $C_{30}H_{32}N_2O_6Br_2CoLi \cdot 2\,H_2O$. Calculated (%): C, 46.30; H, 4.66; N, 3.60. ^{1}H NMR (300 MHz, CD_3OD), δ: 1.16 (d, 6 H, CH_3-Val, *J* = 6.9 Hz); 1.35 (d, 6 H, CH_3-Val, *J* = 6.9 Hz); 2.64—2.80 (m, 2 H, β-H-Val); 2.83, 3.12 (both AB part of ABX system, 4 H, CH_2 of allyl, J_{AB} = 6.1 Hz, J_{AX} = 3.8 Hz, J_{BX} = 5.5 Hz); 5.30 (X part of ABX system, 2 H, =CH of allyl); 4.33 (d, 2 H, α-H-Val, *J* = 3.6 Hz); 4.57—4.68 (m, 4 H, =CH_2 of allyl); 6.88 (d, 2 H, Ar, *J* = 2.7 Hz); 7.49 (d, 2 H, Ar, *J* = 2.7 Hz); 8.45 (s, 2 H, CH=N).

Lithium Λ-bis[*N*-(3-allyl-5-bromosalicylidene)-(*S*)-threoninato]cobaltate ($Li^+[Λ\text{-}5]^-$). The yield was 22%, $[\alpha]_D^{25}$ −5350 (*c* 0.030, MeOH). Found (%): C, 43.19; H, 4.45; N, 3.78. $C_{28}H_{28}N_2O_8Br_2CoLi \cdot 2\,H_2O$. Calculated, (%): C, 42.99; H, 4.12; N, 3.58. ^{1}H NMR (400 MHz, CD_3OD), δ: 1.42 (d, 6 H, CH_3-Thr, *J* = 6.1 Hz); 2.74, 2.76 (both AB part of ABX system, 4 H, CH_2 of allyl, J_{AB} = 14.1 Hz, J_{AX} = 7.8 Hz, J_{BX} = 7.7 Hz); 5.27 (X part of ABX system, 2 H, =CH of allyl); 4.04—4.17 (m, 2 H, β-H-Thr); 4.54 (d, 2 H, α-H-Thr, *J* = 7.6 Hz); 4.69—4.75 (m, 4 H, =CH_2 of allyl); 6.81 (d, 2 H, Ar, *J* = 2.7 Hz); 7.41 (d, 2 H, Ar, *J* = 2.7 Hz); 8.32 (s, 2 H, CH=N).

Lithium Δ-bis[*N*-(3-allyl-5-bromosalicylidene)-(*S*)-threoninato]cobaltate ($Li^+[Δ\text{-}5]^-$). The yield was 65%, $[\alpha]_D^{25}$ −6120 (*c* 0.031, MeOH). Found (%): C, 43.07; H, 4.21; N, 3.64. $C_{28}H_{28}N_2O_8Br_2CoLi \cdot 2\,H_2O$. Calculated (%): C, 42.99; H, 4.12; N, 3.58. ^{1}H NMR (400 MHz, CD_3OD), δ: 1.44 (d, 6 H, CH_3-Thr, *J* = 6.4 Hz); 2.83, 3.09 (both AB part of ABX system, 4 H, CH_2 of allyl, J_{AB} = 12.4 Hz, J_{AX} = 6.8 Hz, J_{BX} = 6.4 Hz); 5.46 (X part of ABX system, 2 H, =CH of allyl); 4.51—4.67 (m, 2 H, β-H-Thr); 4.64 (d, 2 H, α-H-Thr, *J* = 8.4 Hz); 4.70—4.83 (m, 4 H, =CH_2 of allyl); 7.11 (d, 2 H, Ar, *J* = 2.7 Hz); 7.52 (d, 2 H, Ar, *J* = 2.7 Hz); 8.47 (s, 2 H, CH=N).

Lithium Λ-bis[*N*-(3-allyl-5-bromosalicylidene)-(*S*)-tryptophanato]cobaltate ($Li^+[Λ\text{-}6]^-$). The yield was 22%, $[\alpha]_D^{25}$ −7330 (*c* 0.031, MeOH). Found (%): C, 53.12; H, 4.42; N, 5.96. $C_{42}H_{34}N_4O_6Br_2CoLi \cdot 2\,H_2O$. Calculated (%): C, 52.96; H, 4.02; N, 5.88. ^{1}H NMR (400 MHz, CD_3OD), δ: 2.56, 2.61 (both AB part of ABX system, 4 H, CH_2 of allyl, J_{AB} = 15.1 Hz, J_{AX} = 6.4 Hz, J_{BX} = 8.0 Hz); 5.16 (X part of ABX system, 2 H, =CH of allyl); 3.55, 3.76 (both AB part of ABX system, 4 H, CH_2-Trp, J_{AB} = = 11.2 Hz, J_{AX} = 4.4 Hz, J_{BX} = 4.6 Hz); 4.95—5.07 (X part of ABX system, 2 H, α-H-Trp); 4.54—4.68 (m, 4 H, =CH_2 of allyl); 6.63 (d, 2 H, Ar, *J* = 2.7 Hz); 6.68 (d, 2 H, Ar, *J* = 2.7 Hz); 7.13 (t, 2 H, Ar, *J* = 5.8 Hz); 7.16 (s, 2 H, CH=N); 7.18 (t, 2 H, Ar, *J* = 5.6 Hz); 7.44 (d, 2 H, Ar, *J* = 6.3 Hz); 7.97 (d, 2 H, Ar, *J* = 5.4 Hz).

Lithium Δ-bis[*N*-(3-allyl-5-bromosalicylidene)-(*S*)-tryptophanato]cobaltate ($Li^+[Δ\text{-}6]^-$). The yield was 70%, $[\alpha]_D^{25}$ −7450 (*c* 0.030, MeOH). Found (%): C, 53.72; H, 3.42; N, 5.67. $C_{42}H_{34}N_4O_6Br_2CoLi \cdot H_2O$. Calculated (%): C, 53.98; H, 3.88; N, 6.00. ^{1}H NMR (400 MHz, CD_3OD), δ: 3.16, 3.44 (both AB part of ABX system, 4H, CH_2 of allyl, J_{AB} = 5.6 Hz, J_{AX} = 7.2 Hz, J_{BX} = 5.8 Hz); 5.67 (X part of ABX system, 2 H, =CH of allyl); 3.59, 3.78 (both AB part of ABX system, 4 H, CH_2-Trp, J_{AB} = = 14.4 Hz, J_{AX} = 4.2 Hz, J_{BX} = 4.6 Hz); 4.87 (X part of ABX system, 2 H, α-H-Trp); 4.79—4.95 (m, 4 H, =CH_2 of allyl); 6.65 (d, 2 H, Ar, *J* = 2.7 Hz); 6.83 (d, 2 H, Ar, *J* = 2.7 Hz); 7.05 (s, 2 H, CH=N); 7.12 (t, 2 H, Ar, *J* = 7.0 Hz); 7.24 (t, 2 H, Ar, *J* = 6.9 Hz); 7.48 (d, 2 H, Ar, *J* = 8.4 Hz); 7.86 (d, 2 H, Ar, *J* = 7.8 Hz).

Lithium Λ-bis[*N*-(3,5-dichlorosalicylidene)-(*S*)-valinato]cobaltate ($Li^+[Λ\text{-}7]^-$). The yield was 22%, $[\alpha]_D^{25}$ −2985 (*c* 0.035, MeOH). Found (%): C, 42.80; H, 3.44; N, 4.32. $C_{24}H_{22}N_2O_6Cl_4CoLi \cdot 2\,H_2O$. Calculated (%): C, 42.51; H, 3.86; N, 4.13. ^{1}H NMR (300 MHz, CD_3OD), δ: 1.18 (d, 12 H, CH_3-Val, *J* = 6.2 Hz); 2.46—2.55 (m, 2 H, β-H-Val); 4.42 (d, 2 H, α-H-Val, *J* = 7.0 Hz); 7.18 (d, 2 H, Ar, *J* = 2.7 Hz); 7.26 (d, 2 H, Ar, *J* = 3.0); 8.44 (s, 2 H, CH=N).

Lithium Δ-bis[*N*-(3,5-dichlorosalicylidene)-(*S*)-valinato]cobaltate ($Li^+[Δ\text{-}7]^-$). The yield was 70%, $[\alpha]_D^{25}$ −2880 (*c* 0.035, MeOH). Found (%): C, 42.60; H, 3.77; N, 4.26. $C_{24}H_{22}N_2O_6Cl_4CoLi \cdot 2\,H_2O$. Calculated (%): C, 42.51; H, 3.86; N, 4.13. ^{1}H NMR (300 MHz, CD_3OD), δ: 1.15 (d, 6 H, CH_3-Val, *J* = 6.7 Hz); 1.30 (d, 6 H, CH_3-Val, *J* = 6.9 Hz); 2.70—2.80 (m, 2 H, β-H-Val); 4.26 (d, 2 H, α-H-Val, *J* = 8.4 Hz); 7.21 (d, 2 H, Ar, *J* = 2.7 Hz); 7.42 (d, 2 H, Ar, *J* = 3.0 Hz); 8.49 (s, 2 H, CH=N).

Lithium Λ-bis[*N*-(3-methoxysalicylidene)-(*S*)-valinato]cobaltate ($Li^+[Λ\text{-}8]^-$). The yield was 23%, $[\alpha]_D^{25}$ −3460 (*c* 0.031, MeOH). Found (%): C, 49.78; H, 5.93; N, 4.3. $C_{26}H_{30}N_2O_8CoLi \cdot 3.5\,H_2O$. Calculated (%): C, 49.77; H, 5.94; N, 4.46. ^{1}H NMR (300 MHz, CD_3OD), δ: 1.26—1.27 (m, 12 H, CH_3-Val); 2.43—2.54 (m, 2 H, β-H-Val); 3.26 (s, 6 H, OMe); 4.47 (d, 2 H, α-H-Val, *J* = 7.3 Hz); 6.38 (t, 2 H, Ar, *J* = 7.8 Hz); 6.56 (d, 2 H, Ar, *J* = 7.6 Hz); 6.97 (d, 2 H, Ar, *J* = 7.8 Hz); 8.32 (s, 2 H, CH=N).

Lithium Δ-bis[*N*-(3-methoxysalicylidene)-(*S*)-valinato]cobaltate ($Li^+[Δ\text{-}8]^-$). The yield was 65%, $[\alpha]_D^{25}$ −6980 (*c* 0.034, MeOH). Found (%): C, 54.10; H, 5.54; N, 4.92. $C_{26}H_{30}N_2O_8CoLi \cdot H_2O$. Calculated (%): C, 53.62; H, 5.54; N, 4.81. ^{1}H NMR (300 MHz, CD_3OD), δ: 1.18—1.28 (m, 12 H,

CH_3-Val); 2.75—2.86 (m, 2 H, β-H-Val); 3.56 (s, 6 H, OMe); 4.16 (d, 2 H, α-H-Val, J = 8.3 Hz); 6.48 (t, 2 H, Ar, J = 7.8 Hz); 6.64 (d, 2 H, Ar, J = 7.5 Hz); 7.04 (d, 2 H, Ar, J = 8.1 Hz); 8.32 (s, 2 H, CH=N).

Lithium Λ-bis[*N*-(3-methoxysalicylidene)-(*S*)-tryptophanato]cobaltate (Li^+[Λ-9]$^-$). The yield was 17%, $[\alpha]_D^{25}$ −3103 (*c* 0.064, MeOH). Found (%): C, 60.23; H, 4.54; N, 7.28. $C_{38}H_{32}N_4O_8CoLi \cdot H_2O$. Calculated (%): C, 60.33; H, 4.53; N, 7.41. ^{1}H NMR (300 MHz, D_2O—CD_3COCD_3 (1 : 1)), δ: 3.0 (s, 6 H, OMe); 3.4, 3.64 (both AB part of ABX system, 4 H, CH_2-Trp, J_{AB} = 14.0 Hz, J_{AX} = 11.0 Hz, J_{BX} = 2.3 Hz); 5.07 (X part of ABX system, 2 H, α-H-Trp); 6.11 (t, 2 H, Ar, J = 7.8 Hz); 6.26 (d, 2 H, Ar, J = 7.9 Hz); 6.36 (d, 2 H, Ar, J = 6.6 Hz); 6.89 (s, 2 H, Ar); 7.07 (m, 4 H, Ar); 7.16 (s, 2 H, CH=N); 7.39 (d, 2 H, Ar, J = 7.8 Hz); 7.88 (d, 2 H, Ar, J = 7.3 Hz).

Lithium Δ-bis[*N*-(3-methoxysalicylidene)-(*S*)-tryptophanato]cobaltate (Li^+[Δ-9]$^-$). The yield was 58%, $[\alpha]_D^{25}$ −5091 (*c* 0.07, MeOH). Found (%): C, 59.87; H, 4.73; N, 7.29. $C_{38}H_{32}N_4O_8CoLi \cdot H_2O$. Calculated (%): C, 60.33; H, 4.53; N, 7.41. ^{1}H NMR (300 MHz, D_2O—CD_3COCD_3 (1 : 1)), δ: 3.48 (s, 6 H, OMe); 3.43, 3.82 (both AB of ABX system, 4 H, CH_2-Trp, J_{AB} = 13.5 Hz, J_{AX} = 3.5 Hz, J_{BX} =11.4 Hz); 4.84 (X part of ABX system, 2 H, α-H-Trp); 6.2 (d, 4 H, Ar, J = 6.9 Hz); 6.52 (d, 2 H, Ar, J = 6.6 Hz); 6.83 (s, 2 H, Ar); 6.36 (d, 2 H, Ar, J = 6.6 Hz); 7.04 (m, 4 H, Ar); 7.28 (s, 2 H, CH=N); 7.40 (d, 2 H, Ar, J = 7.9 Hz); 7.89 (d, 2 H, Ar, J = 7.8 Hz).

Lithium Λ-bis[*N*-(3-methoxysalicylidene)-(*S*)-*tert*-leucinato]-cobaltate (Li^+[Λ-10]$^-$). The yield was 42%, $[\alpha]_D^{25}$ −4500 (*c* 0.027, MeOH). Found (%): C, 51.89; H, 6.51; N, 4.39. $C_{28}H_{34}N_2O_8CoLi \cdot 3\,H_2O$. Calculated (%): C, 52.02; H, 6.24; N, 4.33. ^{1}H NMR (300 MHz, D_2O), δ: 1.13 (s, 18 H, Me_3C); 3.08 (s, 6 H, OMe); 4.52 (s, 2 H, α-H-Val); 6.43—6.54 (m, 4 H, Ar); 6.99 (d, 2 H, Ar, J = 6.4 Hz); 8.24 (s, 2 H, CH=N).

Lithium Δ-bis[*N*-(3-methoxysalicylidene)-(*S*)-*tert*-leucinato]cobaltate (Li^+[Δ-10]$^-$). The yield was 41%, $[\alpha]_D^{25}$ −5760 (*c* 0.027, MeOH). Found (%): C, 52.19; H, 6.37; N, 4.10. $C_{28}H_{34}N_2O_8CoLi \cdot 3\,H_2O$. Calculated (%): C, 52.02; H, 6.24; N, 4.33. ^{1}H NMR (300 MHz, D_2O), δ: 1.17 (s, 18 H, Me_3C); 3.62 (s, 6 H, OMe); 4.29 (s, 2 H, α-H-Val); 6.22 (t, 2 H, Ar, J = 7.3 Hz); 6.84 (d, 2 H, Ar, J = 7.9 Hz); 7.14 (d, 2 H, Ar, J = 7.9 Hz); 8.34 (s, 2 H, CH=N).

Lithium Λ-bis[*N*-(3-allylsalicylidene)-(*S*)-valinato]cobaltate (Li^+[Λ-11]$^-$). The yield was 19%, $[\alpha]_D^{25}$ −4630 (*c* 0.06, MeOH). Found (%): C, 55.08; H, 5.72; N, 3.90. $C_{30}H_{34}N_2O_6CoLi \cdot 4\,H_2O$. Calculated (%): C, 54.88; H, 6.45; N, 4.27. ^{1}H NMR (300 MHz, CD_3OD), δ: 1.18—1.28 (m, 12 H, CH_3-Val); 2.55 (m, 2 H, β-H-Val); 2.76 (AB part of ABX system, 4 H, CH_2 of allyl, J_{AB} = 15.0 Hz, J_{AX} = 8.0 Hz, J_{BX} = 6.6 Hz); 4.38 (m, 2 H, α-H-Val); 4.64—4.72 (m, 4 H, H_2C=); 5.32 (X part of ABX system, 2 H, =CH); 6.41 (t, 2 H, Ar, J = 7.4 Hz); 6.74 (d, 2 H, Ar, J = 6.5 Hz); 7.22 (d, 2 H, Ar, J = 7.7 Hz); 8.33 (s, 2 H, CH=N).

Lithium Δ-bis[*N*-(3-allylsalicylidene)-(*S*)-valinato]cobaltate (Li^+[Δ-11]$^-$). The yield was 65%, $[\alpha]_D^{25}$ −732 (*c* 0.044, MeOH). Found (%): C, 59.25; H, 6.12; N, 4.29. $C_{30}H_{34}N_2O_6CoLi \cdot 1.25\,H_2O$. Calculated (%): C, 59.36; H, 6.06; N, 4.62. ^{1}H NMR (300 MHz, CD_3OD), δ: 1.22—1.38 (m, 12 H, CH_3-Val); 2.86 (m, 2 H, β-H-Val); 2.92, 3.18 (both AB part of ABX system, 4 H, CH_2 of allyl, J_{AB} = 15.1 Hz, J_{AX} = 5.0 Hz, J_{BX} = 7.2 Hz); 4.46 (m, 2 H, α-H-Val); 4.60—4.73 (m, 4 H, H_2C=); 5.46 (X part of ABX system, 2 H, =CH); 6.48 (t, 2 H, Ar, J = 7.2 Hz); 6.89 (d, 2 H, Ar, J = 7.2 Hz); 7.34 (d, 2 H, Ar, J = 7.9 Hz); 8.50 (s, 2 H, CH=N).

Lithium Λ-bis[*N*-(3-phenylsalicylidene)-(*S*)-valinato]cobaltate (Li^+[Λ-12]$^-$). The yield was 31%, $[\alpha]_D^{25}$ −3455, $[\alpha]_{546}^{25}$ +1180, $[\alpha]_{436}^{25}$ +1455 (*c* 0.066, MeOH). Found (%): C, 60.85; H, 5.64; N, 3.53. $C_{36}H_{34}N_2O_6CoLi \cdot 3\,H_2O$. Calculated (%): C, 60.85; H, 5.67; N, 3.94. ^{1}H NMR (300 MHz, $CDCl_3$—CD_3OD (1 : 1)), δ: 1.21—1.30 (m, 12 H, CH_3-Val); 2.61 (m, 2 H, β-H-Val); 4.34 (d, 2 H, α-H-Val, J = 6.3 Hz); 6.62 (t, 2 H, Ar, J = 7.5 Hz); 7.09 (m, 6 H, Ar); 7.18 (m, 6 H, Ar); 7.44 (d, 2 H, Ar, J = 7.7 Hz); 8.43 (s, 2 H, CH=N).

Lithium Δ-bis[*N*-(3-phenylsalicylidene)-(*S*)-valinato]cobaltate (Li^+[Δ-12]$^-$). The yield was 54%, $[\alpha]_D^{25}$ 0, $[\alpha]_{546}^{25}$ −1550, $[\alpha]_{436}^{25}$ +4138 (*c* 0.06, MeOH). Found (%): C, 62.32; H, 5.42; N, 3.77. $C_{36}H_{34}N_2O_6CoLi \cdot 2\,H_2O$. Calculated (%): C, 62.43; H, 5.53; N, 4.04. ^{1}H NMR (300 MHz, $CDCl_3$—CD_3OD (1 : 1)), δ: 1.21—1.30 (m, 12 H, CH_3-Val); 2.34 (m, 2 H, β-H-Val); 4.28 (m, 2 H, α-H-Val); 6.57 (t, 2 H, Ar, J = 7.5 Hz); 6.96—7.05 (m, 12 H, Ar); 7.40 (d, 2 H, Ar, J = 6.2 Hz); 8.37 (s, 2 H, CH=N).

Addition of TMSCN to aldehydes catalyzed by complexes 1—12 (exemplified by benzaldehyde). The vacuumed Schlenk flask was heated with a heat gun and filled with argon. Then the heating was removed, and the flask was cooled to room temperature in dry argon flow. The catalyst (0.02 mmol), CH_2Cl_2 (1 mL), benzaldehyde (0.1 mL, 0.1 g, 1 mmol), and TMSCN (0.15 mL, 0.111 g, 1.1 mmol) were placed in the flask under argon flow. The reaction mixture was stirred at 25 °C for 1 h under argon and then passed through a small SiO_2 layer to remove the catalyst, and the reaction product was eluted with CH_2Cl_2. The yield of the product was determined using ^{1}H NMR spectroscopy, and its enantiomeric composition was determined by gas chromatography on the chiral stationary phase. The absolute configuration was determined by a comparison of the sign of the optical rotation angle of the obtained product with the literature data.[16]

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