New, Axially Chiral, Bimetallic Catalysts for Asymmetric Alkylation of Aldehydes with Diethylzinc

by **Felix Keller**[1]) and **Andreas Johannes Rippert***

Organisch-chemisches Institut der Universität Zürich, Winterthurerstr. 190, CH-8057 Zürich

Axially chiral bis(salicylidene)ethylenediamine (H_2salen)-type ligands **3** (*cf. Schemes 1* and *3*) are efficient ligands for the enantioselective addition of diethylzinc to aldehydes. There is ample evidence that an active bimetallic catalyst forms an effective chiral pocket (see *Fig. 2*); of a series of first-row transition-metal complexes with these ligands, the most stereoselective were the Co^{II} complexes (see *Fig. 1*). Best ee values as well as the fastest rates (see *Tables 2* and *3*) were obtained with these Co^{II} complexes when an EtO substituent was present at C(3) of the salicylaldehyde residues of ligand **3** (R^1 = EtO), *i.e.*, complex [Co^{II}(**3'h**)] produced up to 93% ee with aromatic aldehydes and 78% ee for aliphatic aldehydes (see *Table 4*).

1. Introduction. – Chiral *N*,*N*′-bis(salicylidene)ethylenediamine (H_2salen) ligands have attracted much interest in asymmetric catalysis. Their complexes with several first-row transition metals have shown high levels of asymmetric induction with several first-row transition metals in the following reactions: *e.g.*, the epoxidation of unfunctionalized olefins (Mn^{III}) [1], the ring opening of *meso*-epoxides with Me_3SiN_3 (Cr^{III}) [2] or carboxylates (Co^{II}) [3], and the ring opening and kinetic resolution of epoxides with water (Co^{II}) [4] as well as hetero-*Diels-Alder* additions (Cr^{III}) [5]. The advantages of these H_2salen ligands are their easy and high-yielding accessibility by a condensation reaction between a diamine and salicylaldehydes (= 2-hydroxybenzaldehydes) and, therefore, an easy tuning of the steric and electronic properties of the ligand. Until now, the chiral diamines used in transition-metal catalysis possessed central chirality. Recently *Meunier et al.* [6] used an axially chiral diamine, namely [1,1′-binaphthalene]-2,2′-diamine, as the chiral backbone of H_2salen-type ligands, which showed, when coordinated to Mn^{III}, low asymmetric induction in the catalyzed epoxidation of unfunctionalized olefins (up to 15% ee). These results are in contrast to those realized with axially chiral phosphine ligands, which are, like binap (a binaphthalene-based diphosphine), the most successful ligands in asymmetric catalysis [7].

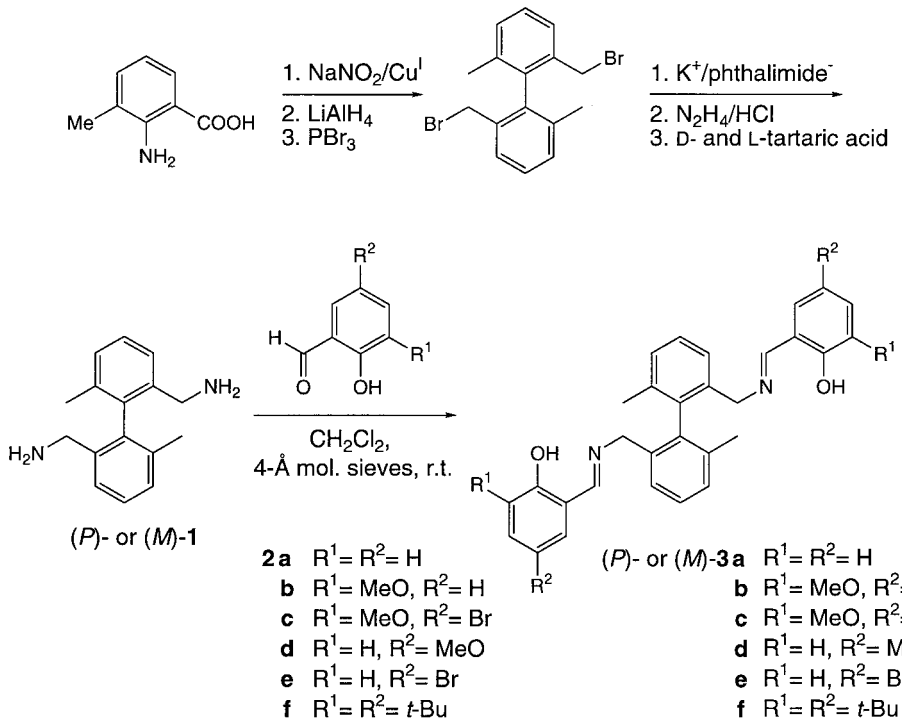
Herein, we wish to report the synthesis of a new axially chiral diamine and the corresponding H_2salen-type ligands, as well as their use as ligands in bimetallic asymmetric transition-metal catalysis. This is exemplified by the widely used C–C bond formation reaction of aldehydes with diethylzinc ($ZnEt_2$) (reviews: [8]) to produce synthetically useful chiral secondary alcohols. The reaction is catalyzed since only a slow reaction takes place between benzaldehyde and $ZnEt_2$ at room temperature. Similar catalyses have been observed with ligand classes such as amino alcohols

[1]) Part of the diploma thesis of *F. K.*, University of Zurich 1997

[9], ferrocene-based amino alcohol [10], polymer-bound [1,1′-binaphtalene]-2,2′-diol [11], or chiral taddol complexes with Ti^{IV} [12], disulfonamides [13], and dihydroxy-disulfonamides [14].

2. Results and Discussion. – The new, axially chiral diamine **1** was synthesized in a straightforward manner in five steps, starting with 3-methylanthranilic acid, including separation into the optical antipodes of (*P*)- or (*M*)-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanamine ((*P*)- or (*M*)-**1**, resp.) with tartaric acid (see *Scheme 1*). Based on preliminary results [15], we optimized the total yield of the sequence up to 30% for one enantiomer with respect to the starting 3-methylanthranilic acid. The corresponding axially chiral H_2salen-type ligands **3** were formed by condensation of **1** with various salicylaldehydes **2**.

Scheme 1



Ligands of type **3** have already been successfully tested in the Mn-catalyzed epoxidation of some unfunctionalized olefins with 3-chloroperbenzoic acid at low temperature [15]. *Cozzi et al.* [16] showed that the addition of $ZnEt_2$ to aromatic aldehydes can be performed and accelerated by *Schiff*-base ligands of the *Jacobsen* type, namely (*S,S*)-*N,N*-bis[3,5-di(*tert*-butyl)salicylidene]cyclohexane-1,2-diamine (ee up to 77%). We screened the reaction of benzaldehydes and $ZnEt_2$ with the new ligands **3**, as outlined in *Scheme 2*. Our first results with these new, axially chiral ligands were generally disappointing in terms of enantioselectivity (*cf. Table 1*).

Scheme 2

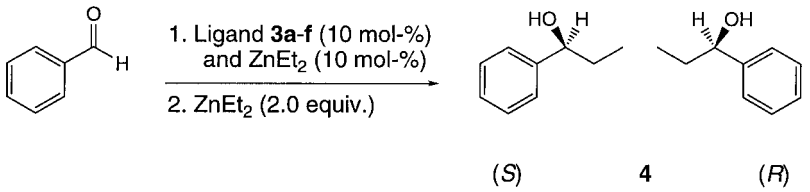


Table 1. *Results of the Reductive Alkylation of Benzaldehyde with $ZnEt_2$*

Entry	Ligand	Configuration of the ligand	R^1	R^2	Solvent	ee [%][a])	Configuration of the secondary alcohol **4**[b])	Yield [%][c])
1	**3a**	(*M*)	H	H	toluene	15	(*S*)	74
2	**3b**	(*M*)	MeO	H	toluene	25	(*S*)	82
3	**3c**	(*P*)	MeO	Br	toluene	19	(*R*)	76
4	**3d**	(*P*)	H	MeO	toluene	4	(*R*)	78
5	**3e**	(*M*)	H	Br	toluene	7	(*S*)	71
6	**3f**	(*M*)	*t*-Bu	*t*-Bu	toluene	5	(*R*)	68
7	**3b**	(*M*)	MeO	H	CH_2Cl_2	24	(*S*)	79
8	**3b**	(*M*)	MeO	H	THF	13	(*S*)	72

[a]) ee Values were determined by HPLC on a chiral column (*Chiracel OD-H*). [b]) The absolute configuration of the formed major stereoisomer was established by comparison of the retention time by HPLC of optically pure (*R*)-1-phenylpropan-1-ol. [c]) Yields were determined by integration of PhC*H*O (10.0 ppm) and PhC*H*(OH)Et (4.55 ppm) in the ^{1}H-NMR.

The best asymmetric induction and the highest yield were reached when we used ligand **3b** with a MeO group at C(3) of the salicylaldehyde residues (R^1 = MeO, R^2 = H; see *Scheme 1*, and for the result *Entry 2*, *Table 1*). By adding an electron-withdrawing group R^2 at C(5) of the salicylaldehyde residues of the ligand **3**, the ee value and the yield decreased to 19% ee and 76%, respectively (*Entry 3*). That the donating group at C(3) is necessary for coordination is obvious from the observation that a MeO group at C(5) reduced the ee value to 4% (*Entry 4*). Sterically demanding groups such as *t*-Bu at C(3) and C(5) showed low asymmetric induction and a low yield (*Entry 6*). This is in contrast to results reported in [16]. However, the ee value was very small, and the absolute configuration of the major alcohol stereoisomer, induced by this ligand (*M*)-**3f**, was opposite to that observed with all the other ligands. Normally, ligands with (*M*) axial chirality induced, as the major stereoisomer, (*S*)-configuration in the formed alcohol. If the donating group at C(3) of the salicylaldehyde residues is necessary, a solvent with good donating properties should influence the ee value. Indeed, no effect was observed when we used a weakly coordinating solvent such as CH_2Cl_2, but with the well coordinating solvent, THF, a remarkable decrease of the ee value was observed (*cf. Entries 7* and *8*).

We regard this finding as evidence that donating groups are probably important for asymmetric induction. In the case of a bimetallic catalyst, it would be possible to optimize the asymmetric induction by changing the transition metal which is first bound to the ligand of type **3b**. The binding of transition metals to the central OˆNˆNˆO binding core of these H_2salen-type ligands **3** will change the geometry and electronic

properties of the complex. The results of this test are summarized in *Fig. 1*. In terms of enantioselectivity, the best value was found with Co^{II} (79% ee). All other tested transition metals showed far lower ee values (4–21% ee). Al^{III} exhibited a reasonable ee value of 38%, but two other achiral products were formed, benzyl alcohol and propiophenone. A possible explanation for this finding is the dehydrogenation of the formed chiral alcohol, leading to propiophenone; the abstracted hydride then attacks the benzaldehyde to form benzyl alcohol.

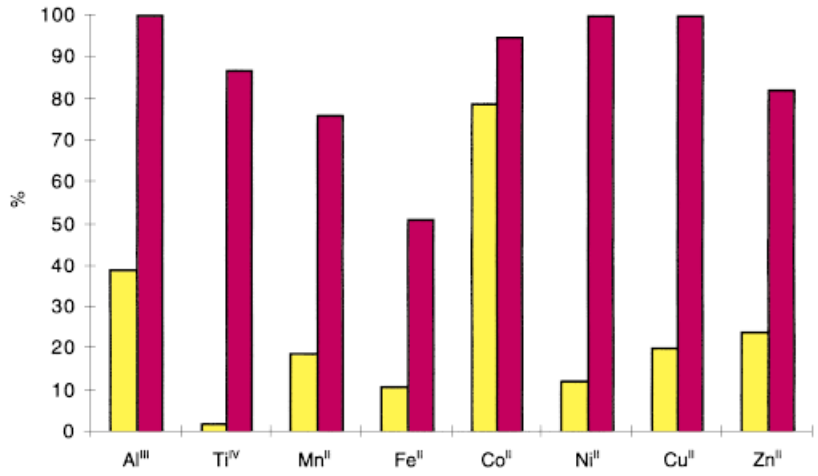


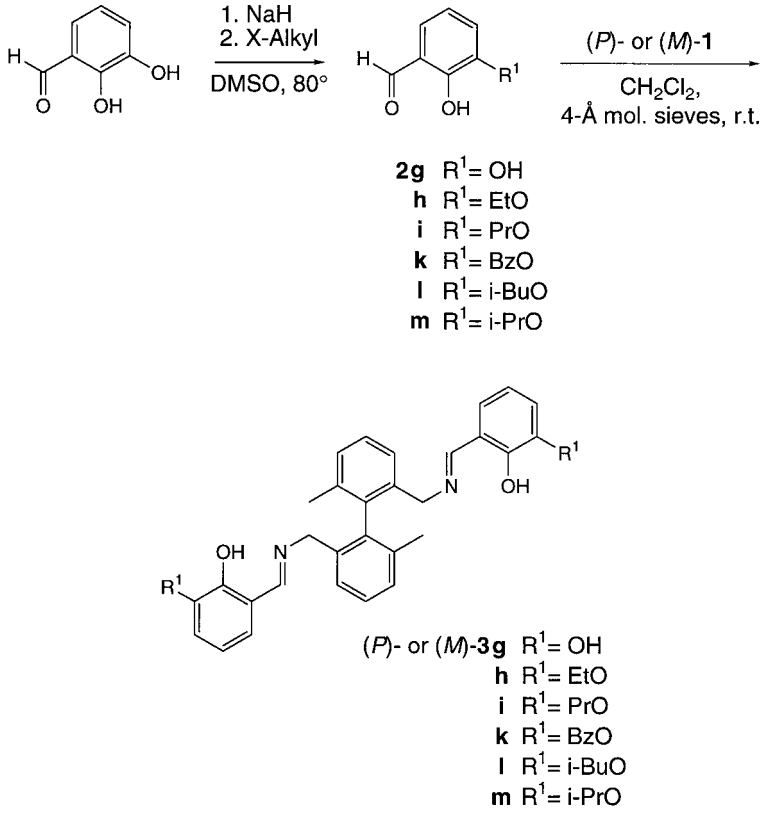
Fig. 1. *Tests of various transition metals of the first-row and Al^{III} with ligand* **3b** *in the reductive alkylation of benzaldehyde with $ZnEt_2$.* Yellow bars: ee values; red bars: conversion of benzaldehyde after 18 h.

Next, we screened the influence of the donating substituents at C(3) of the salicylaldehyde residues by varying the alkyl groups bound to the O-atom. These differently substituted salicylaldehydes were synthesized from 3-hydroxysalicylaldehyde, as outlined in *Scheme 3* [17]. The results of the reductive alkylation of benzaldehyde with $ZnEt_2$ in the presence of the corresponding Co^{II} complexes are summarized in *Table 2*. The Co^{II} complex that showed the highest asymmetric induction as well as the best reactivity was that obtained with ligand **3h** which bears an EtO group at C(3) (90% ee, 61% conversion after 1 h; *Entry 5*, *Table 2*). Sterically more or less demanding groups at C(3) lower both the ee values and the reactivity (*Entries 3* and *6–9*). Also noteworthy is the result obtained with [Co^{II}(**3′a**)][2]) which has no substituent at C(3) of the salicylaldehyde residues of the ligand. No asymmetric induction took place, and the racemic secondary alcohol **4** was formed (*Entry 1*, *Table 2*). This is in contrast to the result obtained with the *in situ* generated [Zn^{II}(**3′a**)] (15% ee; *Entry 1*, *Table 1*) and thus indicates that no metal exchange in [Co^{II}(**3′a**)] took place when an excess of $ZnEt_2$ was added. There were other factors that lowered the asymmetric induction in this catalytic reaction by the new [Co^{II}(ligand **3′**)][2]) complexes: a more ionic donor group at C(3) of the salicylaldehyde residues of ligand

[2]) In the complexes, the ligands **3** are doubly deprotonated, this is symbolized by a primed key number, *i.e.*, **3′**.

3, such as the OH groups in **3g**, showed almost no asymmetric induction (*Entry 2*, *Table 2*). An electron-withdrawing group at C(5) of the salicylaldehyde residues of ligand **3c** was also found to induce a lower asymmetric induction in the secondary alcohol (**4**) as compared to the 5-unsubstituted ligand **3b** (*cf. Entries 4* and *3*, *Table 2*).

Scheme 3



Evidence for a bimetallic catalysis was given by three facts: *i*) as discussed above, no asymmetric induction was observed by the [Co^{II}(**3′a**)] complex in contrast to the Zn^{II} analogue (*cf. Entry 1* in *Table 2* and *Entry 1* in *Table 1*), *ii*) the ee value was temperature-dependent in the Co^{II}-complex-mediated reductive alkylation of benzaldehyde. The highest ee value could be reached when [Co^{II}(**3′b**)] was first stirred with an equimolar amount of $ZnEt_2$ for 30 min at room temperature and then cooled to 0° before additional $ZnEt_2$ and benzaldehyde were added (82% ee). When [Co^{II}(**3′b**)] and an equimolar amount of $ZnEt_2$ were cooled to 0° or heated to 40° from the beginning, the ee values were significantly lower (0°, 67% ee; 40°, 69% ee). Thus, an initial complexation of an equimolar amount of $ZnEt_2$ to the free binding sites of the [Co^{II}(**3′b**)] complex takes place and is crucial. *iii*) Binding studies, carried out by means of a titration of ligand **3b** with $ZnEt_2$ monitored by ^{1}H-NMR spectroscopy, showed that coordination of Zn^{II} took place initially at the central H_2salen-type O^N^N^O core of

Table 2. *Influence of the Alkoxy Substituents in the Reduction of Benzaldehyde with $ZnEt_2$*

Entry	Complex	Configuration of the ligand	R^1	R^2	ee [%][a])	Configuration of the secondary alcohol **4**[b])	Conversion [%][c]) after 1 h
1	[Co^{II}(**3′a**)]	(*M*)	H	H	0	–	14
2	[Co^{II}(**3′g**)]	(*M*)	HO	H	2	(*S*)	15
3	[Co^{II}(**3′b**)]	(*M*)	MeO	H	78	(*S*)	48
4	[Co^{II}(**3′c**)]	(*P*)	MeO	Br	69	(*R*)	42
5	[Co^{II}(**3′h**)]	(*M*)	EtO	H	90	(*S*)	61
6	[Co^{II}(**3′i**)]	(*P*)	PrO	H	75	(*R*)	52
7	[Co^{II}(**3′k**)]	(*M*)	BzO	H	55	(*S*)	35
8	[Co^{II}(**3′l**)]	(*P*)	i-BuO	H	7	(*R*)	8
9	[Co^{II}(**3′m**)]	(*M*)	i-Pro	H	14	(*S*)	15

[a]) ee Values were determined by GC on a chiral column (*Cyclodex B*). [b]) The absolute configuration of the formed major stereoisomer was established by comparison of the retention time by HPLC or GC of optically pure (*R*)-1-phenylpropanol. [c]) Conversion was established by GC, and quantified *vs.* mesitylene as an internal standard.

ligand **3b**. This was established by the disappearance of the ^{1}H-NMR signal (300 MHz, C_6D_6) of the OH group of **3b** at 13.80 ppm and a δ shift of the two H-atoms bound to the C=N group from 7.31 (ligand **3b**) → 6.84 ppm (complex [Zn(**3′b**)]; see *Exper. Part*). Addition of a second equiv. of $ZnEt_2$ could not be established because of the low solubility of the formed complex in C_6D_6 which prevented the recording of suitable ^{1}H-NMR spectra. Thus, we propose the presence of a bimetallic complex (see *Fig. 2*) which acts as a catalyst.

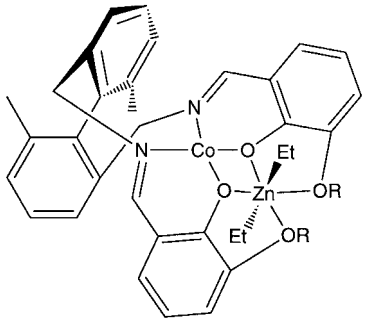


Fig. 2. *Proposed structure for the bimetallic catalyst*

Bimetallic complexes of Co^{II}/Sn^{II} and Ni^{II}/Sn^{II} with similar salen ligands, which have propane-1,3-diamine as the backbone, were characterized by X-ray crystallographic analyses [18]. In these complexes, the first-row transition metal was bound to the central salen O^N^N^O core and the Sn^{II} was coordinated to the O-atoms of the alkoxy groups, as well as to the same O-atoms to which the first-row transition metal was bound. Very recently, another bimetallic complex (Mn^{III}/Cu^{II}) with a salen ligand has been proposed for a catalyst [19] which showed high activities towards H_2O_2 decomposition.

To obtain more information about the rate and selectivity dependence of our bimetallic system, we screened the Co^{II} complexes under different reaction conditions.

The second-order rate law was determined by GC analysis for each set of conditions. The resulting k_2 values are summarized in *Table 3*. The catalyst concentration increased the rate and, slightly, the enantioselectivity (*Entries 1–3*, *Table 3*). Of the tested solvents, toluene produced the highest rate and the best ee values (*Entries 1* and *4–6*). An alkoxy substituent in the salicylaldehyde residues resulted in lower rates as well as lower ee values when a sterically less or more demanding group (see **3b** and **3i**, resp.) than the EtO substituent (see **3b**) was introduced (*Entries 1, 7*, and *8*, *Table 3*; *cf. Table 2*). The dialkylzinc reagents also influence the rate. When using $ZnMe_2$, the reaction with benzaldehyde was *ca.* 10 times slower compared with that obtained using $ZnEt_2$. However, $ZnMe_2$ produced almost the same level of asymmetric induction in the formed alcohol, namely 1-phenylethanol (*Entries 1* and *9* in *Table 3*).

Table 3. *Influence of Various Reaction Conditions on the Rate and Stereoselectivity of the Bimetallic Catalytic System* (Co^{II}/Zn^{II})

Entry	Complex	Concentration of catalyst [mol-%]	Solvent	R^1	X of ZnX_2	ee [a])	$(k_2 \pm \sigma) \cdot 10^{-6}$ [b])
1	$[Co^{II}(\mathbf{3'h})]$	10	toluene	EtO	Et	90	6.40 ± 0.34
2	$[Co^{II}(\mathbf{3'h})]$	5	toluene	EtO	Et	87	1.58 ± 0.06
3	$[Co^{II}(\mathbf{3'h})]$	20	toluene	EtO	Et	91	18.6 ± 0.9
4	$[Co^{II}(\mathbf{3'h})]$	10	hexane	EtO	Et	87	6.00 ± 0.06
5	$[Co^{II}(\mathbf{3'h})]$	10	benzene	EtO	Et	87	2.29 ± 0.13
6	$[Co^{II}(\mathbf{3'h})]$	10	PhCl	EtO	Et	87	2.26 ± 0.05
7	$[Co^{II}(\mathbf{3'b})]$	10	toluene	MeO	Et	78	3.60 ± 0.11
8	$[Co^{II}(\mathbf{3'i})]$	10	toluene	PrO	Et	75	1.26 ± 0.03
9	$[Co^{II}(\mathbf{3'h})]$	10	toluene	EtO	Me	88	0.50 ± 0.01

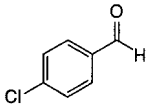
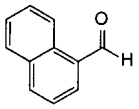
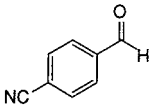
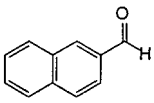
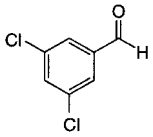
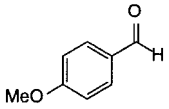
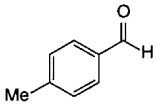
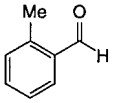
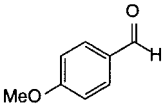
[a]) ee Values were determined by GC on a chiral column (*CyclodexB*). [b]) Conversion was established by GC, and quantified *vs.* mesitylene as an internal standard.

With the most selective and reactive complex $[Co^{II}(\mathbf{3'h})]$, several aldehydes were tested and showed the trends summarized in *Table 4*. The best ee values were observed with substituted benzaldehydes possessing electron-withdrawing groups (*cf. Entries 1–3*, *Table 4*); donating groups showed lower asymmetric induction (*Entries 4* and *6*). Also, *ortho*-substituents produced lower ee values, when compared with the same substituents in the *para*-position (*Entries 5* and *6*). Naphthalene-1-carbaldehyde and -2-carbaldehyde showed similar enantioselectivities to benzaldehyde (*Entries 7* and *8*). Even aliphatic aldehydes could be reduced with reasonable asymmetric induction (*Entries 9* and *10*), except for the sterically demanding pivalaldehyde (= 2,2-dimethylpropanal) which showed a low ee as well as low conversions.

The stereochemical outcome of the reaction between aldehydes and both $ZnEt_2$ and $ZnMe_2$ in the presence of the new complexes $[Co^{II}(\mathbf{3'})]$ can be explained by the structure proposed in *Fig. 2*. Complexation of the aldehyde takes place at the Co^{II} ion. If we use a ligand with (*M*)-chirality, the aldehyde will be oriented by steric and π-π interactions in such a way that the *si*-face is pointing towards the 3-substituent of the salicylaldehyde residue, where the $ZnEt_2$ can be complexed (*cf. Fig. 3*).

3. Conclusion. We could show that the new axially chiral OˆNˆNˆO ligands **3** of the H_2salen type are potential ligands for asymmetric transition-metal catalysis. Good

Table 4. *Reductive Alkylation of Various Aldehydes with $ZnEt_2$ and [Co^{II}(**3'h**)]* (10 mol-%) *as the Catalyst*

Entry	Aldehydes	ee [%][a])	Conversion [%][b]) after 1 h	*Entry*	Aldehydes	ee [%][a])	Conversion [%][b]) after 1 h
1		91	82	*7*		89	32
2		93	> 99	*8*		89	52
3		93	> 99	*9*		75	19
4		88	30	*10*		79	25
5		72	27	*11*		36	traces
6		82	14				

[a]) ee Values were determined by GC on a chiral column (*CyclodexB*); in the case of aliphatic alcohols, their corresponding acetyl derivatives were analyzed. [b]) Conversion was established by GC and quantified *vs.* mesitylene as an internal standard.

levels of asymmetric induction were found in the reductive alkylation of aldehydes with $ZnEt_2$, when an alkoxy group is attached at C(3) of the salicylaldehyde residues of ligand **3**. There is evidence for an active bimetallic catalyst, with Co^{II} in the central

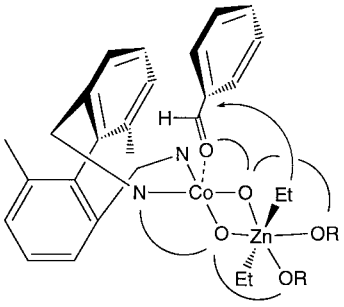


Fig. 3. *Orientation of aldehydes at the site of the bimetallic catalyst with* (M)*-chirality*

salen-type O^N^N^O core of the ligand, and in which the second transition metal Zn^{II} is coordinated to the two additional donor groups of the alkoxy substituents at C(3) of the salicylaldehyde residues of the ligand, as well as to the same two O-atoms of the central salen-type core which are also bound to the Co^{II} atom, these O-donors bridging the two metal atoms (*cf. Fig. 2*). Therefore, the reaction of the aldehyde and $ZnEt_2$ takes place in a chiral pocket, comparably to many highly enantioselective enzymatic reactions that occur in a deeply embedded active site.

Further studies are in progress to use this bimetallic system in other transformations.

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Experimental Part

1. *General*. All catalytic reactions were performed under N_2. All solvents were distilled under N_2 prior to their use. THF was purified over Al_2O_3 (basic, act. I). 3-Methyl-2-nitrobenzoic acid (*Fluka*, *purum*) was reduced with H_2 and Pd/C (*Fluka*) to the corresponding 2-amino-3-methylbenzoic acid. Benzaldehyde (*Fluka*, *puriss.*) was distilled under N_2. $ZnEt_2$ (*Fluka*, *purum*; 1.1M in toluene), $[Co(AcO)_2]$. $4\,H_2O$ (*Fluka*, *purum p.a.*), $[Mn(AcO)_2]\cdot 4\,H_2O$ (*Fluka*, *purum p.a.*), $FeCl_2$ (*Fluka*, *purum*), $[Ni(AcO)_2]$. $4\,H_2O$ (*Fluka*, *purum p.a.*), $[Cu(AcO)_2]\cdot H_2O$ (*Fluka*, *puriss p.a.*), $AlCl(Et)_2$ (*Fluka*, *pract.* 1M in hexane), and $Ti(i\text{-}PrO)_4$ (*Aldrich*) were used without further purification. GC: *CE Instruments GC-8000Top* apparatus equipped with a *CyclodexB* column (30 m × 0.25 mm, 0.25 μm; *J & W Scientific*) for the determination of the ee values and the conversion in catalytic reactions. HPLC: *LichroCart*®-(*S,S*)-*Whelk-O-1* column (244 mm × 4 mm, 5 μm; *Merck*, No. 1.50164) with *LiChrospher® 100 Diol* as a precolumn (4 mm × 4 mm, 5 μm; *Merck*, No. 1.50960) for determination of the separation of (*M*)- and (*P*)-**1**; and *Chiracel OD-H* column (250 mm × 4.6 mm, 5 μm) with *Spherisorb Si* (50 mm × 4.6 mm, 5 μm; *Daicel*) as a precolumn for the determination of the ee value of **4**; UV photodiode-array detector (*Jasco*, model *MD-910*) and *Milton-Roy* pump (model *CM 4000*). M.p.: *Büchi 510* melting point apparatus or apparatus constructed and assembled by *K. Hochreutener*, University of Zurich; not corrected. Optical rotations: *Perkin Elmer-MC-941* polarimeter. CD: *Jasco-J-715* spectropolarimeter; λ in nm ($\Delta\varepsilon$). ^{1}H- and ^{13}C-NMR: *Bruker-AC-300*, *-ARX-300*, and *-AMX-600* spectrometers; δ in ppm rel. to an internal standard ($\delta(SiMe_4) = 0$ ppm).

1. *(*M*)- or (*P*)-6,6′-Dimethyl[1,1′-biphenyl]-2,2′-dimethanamine* ((*M*)- or (*P*)-**1**). 2-Amino-3-methylbenzoic acid was diazotized with $NaNO_2$ (*Fluka*), and the coupling to the biphenyl was achieved by a Cu^I salt derived from $CuSO_4$ (see [20] [21]) (yield after crystallization from acetone, 78%). Reduction of *(*MP*)-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dicarbocylic acid* with $LiAlH_4$ (*Fluka*) in Et_2O (yield after crystallization from toluene, 95%) followed by bromination with PBr_3 (*Fluka*) in toluene led to *(*MP*)-2,2′-bis(bromomethyl)-6,6′-dimethyl[1,1′-biphenyl]* (yield after crystallization from EtOH, 93%). Subsequent exchange of the Br-atoms with potassium phthalimide (*Fluka*) in DMF (yield, 93%) and *Gabriel* synthesis with hydrazine (*Fluka*) in EtOH and acidic workup (conc. HCl soln.) gave (*MP*)-**1** (yield of crude product, 86%). Separation of the enantiomers was achieved by two crystallizations with the corresponding tartaric acid in EtOH/0.001M HCl: 57% (crystallization) of (*P*)-**1** obtained with L-tartaric acid (*Fluka*) and 53% (crystallization) of (*M*)-**1** obtained with D-tartaric acid (*Fluka*). Overall yield: 31% of (*P*)-**1** and 29% of (*M*)-**1**.

*Data of (*P*)-***1***:* M.p. 69° (EtOH). $[\alpha]_D^{20} = -21.0$ ($c = 1.0$, EtOH). CD ($c = 3.08 \cdot 10^{-5}$ M, hexane): 193.2 (−17.30); 208.8 (5.76); 218.1 (4.52, sh); 242.6 (−1.24). IR (KBr): 3354*m* (br.), 3019*m*, 2917*m*, 1578*s*, 1462*s*, 1377*m*, 1321*m*, 1166*w*, 1034*w*, 1002*w*, 935*w*, 886*w*, 821*w*, 761*s*, 598*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.31 (*dd*, $^3J =$ 7.7, $^4J = 1.8$, H−C(3,3′)); 7.27 (*t*, $^3J = 7.6$, H−C(4,4′)); 7.17 (*dd*, $^3J = 7.0$, $^4J = 1.7$, H−C(5,5′)); 3.36, 3.29 (*AB*, $J_{AB} = 14.3$, 2 CH_2NH$_2$); 1.82 (*s*, 2 Me); 1.30 (br. *s*, 2 NH$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): 140.5 (C(2,2′)); 137.6 (C(1,1′)); 135.7 (C(6,6′)); 128.5 (C(5,5′)); 127.6 (C(4,4′)); 125.0 (C(3,3′)); 44.1 (CH_2NH_2); 19.8 (Me). ^{1}H-NOE (300 MHz, $CDCl_3$): 1.82 (Me) → 7.17 (*s*, H−C(5,5′)). ^{1}H,^{13}C-HETCOR (300 MHz, $CDCl_3$): 7.31 → 125.0; 7.27 → 127.6; 7.17 → 128.5; 3.36 and 3.29 → 44.1; 1.82 → 19.8. ^{1}H, ^{13}C-COLOC (300 MHz, $CDCl_3$): 7.31 → 137.6 (*w*), 128.5 (*m*); 7.27 → 140.5 (*m*), 135.7 (*w*); 7.17 → 137.6 (*m*), 125.0 (*m*), 19.8 (*m*); 3.36

and 3.29 → 140.5 (*m*), 137.6 (*w*), 125.0 (*m*); 1.82 → 137.6 (*m*), 135.7 (*s*), 128.5 (*m*). Anal. calc. for $C_{16}H_{20}N_2 \cdot C_4H_6O_6$ (390.44): C 61.53, H 6.71, N 7.17; found: C 61.23, H 6.68, N 7.05.

*Data of (*M*)-***1***:* M.p. 69° (EtOH). $[\alpha]_D^{20} = +21.1$ ($c = 1.0$, EtOH). CD ($c = 3.52 \cdot 10^{-5}$ M, hexane): 193.1 (17.10); 208.8 (– 5.71); 218.4 (– 4.43, *sh*); 242.6 (1.23).

2. *Determination of the Optical Purity of the Enantiomers (*P*)- and (*M*)-***1***.* To a clear soln. of (*P*)- or (*M*)-**1** (50 mg, 0.21 mmol) in CH_2Cl_2 (10 ml) and a few drops of pyridine, pivaloyl chloride (2,2-dimethylpropanoyl chloride; 0.05 ml, 0.43 mmol) was added (→ white precipitation). The mixture was stirred at r.t. for 1 h and then extracted with 1M HCl and sat. $NaHCO_3$ soln. The org. phase was dried (Na_2SO_4) and evaporated. The colorless residue of *(*P*)-* or *(*M*)-*N,N′*-({6,6′-dimethyl[1,1′-biphenyl]-2,2′-diyl}bis(methylene))[2,2-dimethylpropanamide]* was examined by HPLC ((*S,S*)-*Whelk-O-1* column, hexane/EtOH 95:5, flow 1 ml): t_R 16.4 (*P*) and 19.0 min (*M*); $\alpha = 1.19$.

3. *Optically Pure H_2Salen-Type Ligands: General Procedure.* To the colorless soln. of (*P*)- or (*M*)-**1** (1 mmol) in CH_2Cl_2 (10 ml) in the presence of 4-Å molecular sieves, the corresponding salicylaldehyde (2 mmol-equiv.) was added (immediate color change to yellow). After 1 h stirring at r.t., the yellow soln. was filtered over silica gel (1% Et_3N) and evaporated. The residue was dried and crystallized (EtOH).

*(*M*)-*N,N′*-Bis[(2-hydroxyphenyl)methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanamine* (**3a**): M.p. 89° (EtOH). CD ($c = 1.06 \cdot 10^{-5}$ M, EtOH): 211 (11.14), 228 (– 13.77), 262 (– 11.81), 280 (– 3.85, sh), 332 (– 0.35). IR (KBr): 3055*m*, 2924*m*, 2850*m*, 1625*s*, 1579*m*, 1494*s*, 1460*s*, 1442*m*, 1409*m*, 1384*m*, 1334*m*, 1280*s*, 1209*m*, 1150*m*, 1116*m*, 1039*m*, 991*m*, 888*w*, 817*m*, 797*m*, 785*m*, 757*s*, 655*m*, 570*w*, 528*w*, 474*w*, 458*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.32 (br. *s*, 2 OH); 7.62 (*s*, 2 N=C–H); 7.34 – 7.23 (*m*, 8 arom. H); 7.00 (*dd*, $^3J = 7.6$, $^4J = 1.7$, 2 arom. H); 6.89 (*dt*, $^3J = 7.6$, $^4J = 1.0$, 2 arom. H); 4.33, 4.16 (*AB*, $J_{AB} = 14.0$, 2 CH_2N); 1.89 (*s*, 2 Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.5; 161.0; 138.0; 136.2; 135.3; 132.2; 131.5; 129.6; 127.7; 126.8; 118.6; 118.5; 116.9; 62.2 (CH_2N); 19.8 (Me). Anal. calc. for $C_{30}H_{28}N_2O_2$ (448.57): C 80.33, H 6.29, N 6.25; found: C 80.48, H 6.47, N 6.05.

*(*M*)-*N,N′*-Bis[(2-hydroxy-3-methoxyphenyl)methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanamine* (**3b**): M.p. 78° (EtOH). CD ($c = 9.67 \cdot 10^{-6}$ M, EtOH): 213 (1.72), 229 (– 4.62), 272 (– 8.45). IR (KBr): 3443*w*, (br.), 3060*w*, 3000*w*, 2923*m*, 1629*s*, 1464*s*, 1381*m*, 1335*m*, 1254*s*, 1169*w*, 1080*m*, 1045*m*, 973*m*, 950*w*, 839*m*, 780*m*, 736*s*, 644*w*, 570*w*, 516*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.83 (br. *s*, 2 OH); 7.63 (*s*, 2 N=C–H); 7.30 – 7.21 (*m*, 6 arom. H); 6.84 (*dd*, $^3J = 7.9$, $^4J = 1.5$, 2 arom. H); 6.71 (*d*, $^3J = 8.0$, 2 arom. H); 6.63 (*dd*, $^3J = 7.9$, $^4J = 1.5$, 2 arom. H); 4.33, 4.15 (*AB*, $J_{AB} = 14.0$, 2 CH_2N); 3.87 (*s*, 2 MeO); 1.89 (*s*, 2 Me). ^{1}H-NMR (300 MHz, C_6D_6): 13.80 (br. *s*, 2 OH); 7.31 (*s*, 2 N=C–H); 7.17 (*d*, $^3J = 7.2$, 2 arom. H); 7.09 (*t*, $^3J = 7.2$, H–C(4,4′)); 7.01 (*d*, $^3J = 7.2$, 2 arom. H); 6.68 – 6.52 (*m*, 6 arom. H); 4.04, 3.93 (*AB*, $J_{AB} = 14.2$, 2 CH_2N); 3.49 (*s*, 2 MeO); 1.75 (*s*, 2 Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.7; 151.8; 148.3; 137.8; 136.2; 135.2; 129.6; 127.9; 126.7; 123.1; 118.4; 117.7; 113.9; 61.5 (CH_2N); 56.0 (MeO); 19.8 (Me). Anal. calc. for $C_{32}H_{32}N_2O_4$ (508.62): C 75.57, H 6.34, N 5.51; found: C 75.42, H 6.31, N 5.47.

*(*P*)-*N,N′*-Bis[(5-bromo-2-hydroxy-3-methoxyphenyl)methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′dimethanamine* (**3c**): M.p. 75° (EtOH). CD ($c = 1.01 \cdot 10^{-5}$ M, EtOH): 211 (– 15.45), 225 (12.30), 248 (– 8.64), 270 (– 7.13), 342 (1.29). IR (KBr): 3443*w* (br.), 2933*m*, 2848*m*, 1631*s*, 1574*m*, 1472*s*, 1442*s*, 1395*m*, 1335*m*, 1272*s*, 1252*s*, 1099*m*, 1048*m*, 977*m*, 950*w*, 910*w*, 865*m*, 840*m*, 763*m*, 736*m*, 692*w*, 577*w*, 512*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.87 (br. *s*, 2 OH); 7.54 (*s*, 2 N=C–H); 7.32 – 7.24 (*m*, 6 arom. H); 6.90 (*d*, $^4J = 2.2$, 2 arom. H); 6.73 (*d*, $^4J = 2.2$, 2 arom. H); 4.35, 4.12 (*AB*, $J_{AB} = 14.3$, CH_2N); 3.86 (*s*, 2 MeO); 1.90 (*s*, 2 Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 164.5; 151.7; 149.4; 137.8; 136.3; 129.8; 128.1; 126.7; 124.8; 118.9; 116.9; 109.0; 61.2 (CH_2N); 56.3 (MeO); 19.8 (Me).

*(*P*)-*N,N′*-Bis[(2-hydroxy-5-methoxyphenyl)methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′dimethanamine* (**3d**): M.p. 73° (EtOH). CD ($c = 1.03 \cdot 10^{-5}$ M, EtOH): 219 (– 16.35), 240 (22.75), 263 (10.91), 359 (– 1.06). IR (KBr): 3444*w* (br.), 2998*m*, 2922*m*, 1635*s*, 1590*s*, 1492*s*, 1463*s*, 1370*m*, 1332*s*, 1270*s*, 1225*s*, 1195*m*, 1158*s*, 1037*s*, 934*w*, 911*w*, 847*m*, 764*s*, 680*w*, 666*w*, 631*w*, 587*w*, 462*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 12.75 (br. *s*, 2 OH); 7.59 (*s*, 2 N=C–H); 7.32 – 7.22 (*m*, 6 arom. H); 6.85 (*m*, 4 arom. H); 6.52 (*d*, $^4J = 2.5$, 2 arom. H); 4.33, 4.15 (*AB*, $J_{AB} = 14.0$, 2 CH_2N); 3.72 (*s*, 2 MeO); 1.89 (*s*, 2 Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.3; 155.0; 151.8; 137.9; 136.2; 135.3; 129.5; 127.8; 126.7; 119.1; 118.3; 117.7; 115.0; 62.2 (CH_2N); 55.8 (MeO); 19.7 (Me).

*(*M*)-*N,N′*-Bis[(5-bromo-2-hydroxyphenyl)methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanamine* (**3e**): M.p. 87° (EtOH). CD ($c = 1.06 \cdot 10^{-5}$ M, EtOH): 216 (26.31), 234 (– 26.81), 253 (– 10.10), 318 (– 0.80), 349 (0.23). IR (KBr): 3443*w* (br.), 2919*m*, 1631*s*, 1570*m*, 1475*s*, 1441*m*, 1384*m*, 1362*m*, 1328*w*, 1279*s*, 1237*w*, 1203*m*, 1181*m*, 1129*w*, 1076*m*, 1046*m*, 985*w*, 956*w*, 891*w*, 880*w*, 820*s*, 795*m*, 764*m*, 688*m*, 625*m*, 553*w*, 464*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.26 (br. *s*, 2 OH); 7.56 (*s*, 2 N=C–H); 7.36 – 7.23 (*m*, 8 arom. H); 7.10 (*d*, $^4J = 2.2$, 2 arom. H); 6.80 (*d*, $^3J = 8.7$, 2 arom. H); 4.33, 4.17 (*AB*, $J_{AB} = 14.0$, 2 CH_2N); 1.89 (*s*, 2 Me). ^{13}C-NMR

(75 MHz, $CDCl_3$): 164.2; 159.9; 137.9; 136.3; 134.9; 134.8; 133.4; 129.7; 128.0; 126.8; 119.9; 118.9; 109.9; 62.1 (CH_2N); 19.7 (Me). Anal. calc. for $C_{30}H_{26}Br_2N_2O_2$ (606.36): C 59.43, H 4.32, N 4.62; found: C 59.30, H 4.34, N 4.60.

*(*M*)*-N,N′-*Bis[[3,5-di(*tert*-butyl)-2-hydroxyphenyl]methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanamine* (**3f**): M.p. 94° (EtOH). IR (KBr): 3418*w*, 2959*s*, 2868*s*, 1629*s*, 1596*m*, 1467*s*, 1441*s*, 1392*m*, 1361*m*, 1329*m*, 1273*m*, 1251*s*, 1234*m*, 1202*m*, 1173*m*, 1132*w*, 1042*w*, 947*w*, 879*m*, 828*m*, 801*m*, 772*m*, 761*m*, 731*w*, 712*w*, 644*w*, 518*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.70 (br. *s*, 2 OH); 7.60 (*s*, 2 N=C−H); 7.35–7.21 (*m*, 8 arom. H); 6.84 (*d*, ^4J = 2.4, 2 arom. H); 4.32, 4.18 (*AB*, J_{AB} = 13.9, 2 CH_2N); 1.89 (*s*, 2 Me); 1.42 (*s*, 4 *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.6; 158.0; 139.9; 138.1; 136.5; 136.3; 135.7; 129.5; 127.7; 126.8; 126.2; 117.8; 62.2 (CH_2N); 34.9; 34.2; 29.4 (Me_3C); 19.7 (Me).

*(*M*)*-N,N′-*Bis[(2,3-dihydroxyphenyl)methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanamine* (**3g**): M.p. 95° (EtOH). CD ($c = 6.99 \cdot 10^{-5}$ M, EtOH): 212 (0.45, sh), 226 (−1.36), 250 (0.75), 277 (−3.80), 306 (−0.74, sh), 333 (0.38). IR (KBr): 3375*m*, 3060*m*, 2919*m*, 1634*s*, 1546*m*, 1464*s*, 1381*s*, 1204*s*, 1164*s*, 1028*m*, 850*m*, 802*w*, 783*m*, 737*s*, 569*w*, 495*w*, 470*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.70 (br. *s*, 2 OH); 7.66 (*s*, 2 N=C−H); 7.37–7.23 (*m*, 6 arom. H); 6.92–6.89 (*m*, 2 arom. H), 6.59–6.56 (*m*, 2 arom. H), 4.32, 4.27 (*AB*, J_{AB} = 14.3, 2 CH_2N); 1.95 (*s*, 2 Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.3; 156.1; 146.6; 137.5; 136.1; 134.4; 130.1; 128.3; 126.3; 122.1; 116.8; 115.8; 59.0 (CH_2N); 19.6 (Me).

*(*M*)*-N,N′-*Bis[(3-ethoxy-2-hydroxyphenyl)methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanamine* (**3h**): M.p. 57° (EtOH). CD ($c = 6.26 \cdot 10^{-5}$ M, EtOH): 198 (11.11), 229 (−5.17), 243 (−0.91, sh), 250 (−0.49), 273 (−6.93), 330 (0.37). IR (KBr): 3443*w*, 3060*w*, 2978*m*, 2881*m*, 1628*s*, 1582*m*, 1465*s*, 1382*m*, 1335*m*, 1272*s*, 1251*s*, 1175*m*, 1115*m*, 1079*m*, 1045*m*, 952*w*, 891*m*, 833*m*, 778*s*, 762*m*, 736*s*, 646*w*, 572*w*, 509*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.83 (br. *s*, 2 OH); 7.64 (*s*, 2 N=C−H); 7.33–7.21 (*m*, 6 arom. H); 6.86 (*dd*, ^3J = 7.7, ^4J = 1.7, 2 arom. H), 6.70 (*t*, ^3J = 7.7, 2 arom. H); 6.64 (*dd*, ^3J = 7.7, ^4J = 1.7, 2 arom. H), 4.31, 4.15 (*AB*, J_{AB} = 14.2, 2 CH_2N); 4.07 (*q*, ^3J = 7.0, 2 MeC*H*$_2$O); 1.88 (*s*, 2 Me); 1.46 (*t*, ^3J = 7.0, 2 *Me*CH_2O). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.6; 152.0; 147.6; 137.8; 136.2; 135.2; 129.6; 127.9; 126.8; 123.1; 118.6; 117.8; 115.5; 64.5; 61.5; 19.8 (Me); 14.9 (*Me*CH_2O). Anal. calc. for $C_{34}H_{36}N_2O_4$ (536.68): C 76.09, H 6.76, N 5.22; found: C 75.82, H 6.68, N 5.15.

(P)-N,N′-*Bis[(2-hydroxy-3-propoxyphenyl)methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanamine* (**3i**): M.p. 55° (EtOH). CD ($c = 4.74 - 10^{-5}$ M, EtOH): 198 (−11.35), 213 (−0.45, sh), 230 (5.44), 245 (0.64, sh) 252 (0.15), 246 (−0.15), 273 (6.86), 302 (1.21, sh), 334 (−0.98). IR (KBr): 3424*w*, 3060*w*, 2963*m*, 2934*m*, 2876*m*, 1629*s*, 1582*m*, 1464*s*, 1381*m*, 1335*m*, 1253*s*, 1174*w*, 1080*m*, 1047*m*, 977*w*, 943*m*, 910*w*, 843*m*, 779*m*, 735*s*, 641*w*, 571*w*, 512*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.83 (br. *s*, 2 OH); 7.63 (*s*, 2 N=C−H); 7.31–7.20 (*m*, 6 arom. H); 6.86 (*dd*, ^3J = 7.8, ^4J = 1.6, 2 arom. H); 6.70 (*t*, ^3J = 7.8, 2 arom. H); 6.63 (*dd*, ^3J = 7.8, ^4J = 1.7, 2 arom. H); 4.30, 4.14 (*AB*, J_{AB} = 14.2, 2 CH_2N); 3.96 (*t*, ^3J = 6.7, 2 MeCH_2CH_2O); 1.88 (*s*, 2 Me); 1.86 (*sext.*, ^3J = 7.1, 2 MeCH_2CH_2O); 1.04 (*t*, ^3J = 7.4, 2 *Me*CH_2CH_2O). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.7; 152.1; 147.8; 137.8; 136.2; 135.3; 129.5; 127.9; 126.8; 123.2; 118.6; 117.7; 115.7; 70.6; 61.5; 22.6; 19.8 (Me); 10.5.

*(*M*)*-N,N′-*Bis[[2-hydroxy-3-(phenylmethoxy)phenyl]methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanamine* (**3k**): M.p. 55° (EtOH). CD ($c = 4.66 \cdot 10^{-5}$ M, EtOH): 213 (4.99), 229 (1.89), 241 (−0.71), 246 (−0.15), 252 (−0.55), 274 (5.18), 295 (2.32, sh), 333 (−1.35). IR (KBr): 3440*m*, 3060*m*, 3029*m*, 2877*m*, 1628*s*, 1497*m*, 1461*s*, 1376*m*, 1334*m*, 1252*s*, 1172*m*, 1083*m*, 1069*m*, 1044*m*, 975*m*, 910*m*, 845*m*, 778*m*, 736*s*, 696*s*, 649*w*, 576*w*, 508*w*, 469*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.83 (br. *s*, 2 OH); 7.63 (*s*, 2 N=C−H); 7.44 (*d*, ^3J = 7.1, 2 arom. H); 7.37–7.20 (*m*, 12 arom. H); 6.90–6.84 (*m*, 2 arom. H), 6.65–6.63 (*m*, 4 arom. H); 5.13 (*s*, 2 PhCH_2O), 4.32, 4.16 (*AB*, J_{AB} = 14.1, 2 CH_2N); 1.89 (*s*, 2 Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.7; 152.5; 147.3; 137.9; 137.3; 136.3; 135.2; 129.6; 128.5; 127.9; 127.8; 127.4; 126.8; 125.7; 123.9; 118.8; 117.7; 117.1; 71.1; 61.5; 19.7 (Me).

*(*P*)*-N,N′-*Bis[[(2-hydroxy-3-(2-methylpropoxy)phenyl]methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanamine* (**3l**): M.p. 42° (EtOH). CD ($c = 4.98 \cdot 10^{-5}$ M, EtOH): 213 (−2.07, sh), 230 (2.96), 250 (−0.08), 274 (6.23), 302 (1.09, sh), 335 (−1.00). IR (KBr): 3417*w* (br.), 3061*w*, 2956*m*, 2871*m*, 1629*s*, 1583*m*, 1462*s*, 1392*m*, 1334*m*, 1251*s*, 1175*m*, 1077*m*, 1044*m*, 984*m*, 948*w*, 843*m*, 778*m*, 735*s*, 649*w*, 566*w*, 508*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.73 (br. *s*, 2 OH); 7.59 (*s*, 2 N=C−H); 7.30–7.19 (*m*, 6 arom. H); 6.85 (*dd*, ^3J = 7.8, ^4J = 1.5, 2 arom. H); 6.69 (*t*, ^3J = 7.8, 2 arom. H), 6.61 (*dd*, ^3J = 7.8, ^4J = 1.6, 2 arom. H); 4.31, 4.13 (*AB*, J_{AB} = 14.1, 2 CH_2N); 3.75 (*d*, ^3J = 6.7, 2 Me_2CHCH_2O); 2.16 (*sept.*, ^3J = 6.7, 2 Me_2C*H*CH_2O); 1.88 (*s*, 2 Me); 1.03 (*d*, ^3J = 6.7, 2 *Me*$_2$CHCH_2O). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.7 (CH=N); 152.1; 147.9; 137.8; 136.1; 135.2; 129.5; 127.8; 126.7; 123.1; 118.5; 117.6; 115.8; 75.6 (Me_2CHCH_2O); 61.6 (CH_2); 28.2 (Me_2*C*HCH_2O); 19.7 (Me); 19.3, 19.2 (*Me*$_2$CHCH_2O).

*(*M*)*-N,N′-*Bis[[2-hydroxy-3-(1-methylethoxy)phenyl]methylidene]-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanamine* (**3m**): M.p. 51° (EtOH). CD ($c = 4.74 \cdot 10^{-5}$ M, EtOH): 196 (11.16), 213 (1.37, sh), 228 (−3.34), 244 (−0.85), 272 (−6.43), 304 (−0.83, sh), 335 (−0.74). IR (KBr): 3406*w*, 3061*w*, 2974*m*, 2921*m*, 1629*s*, 1462*s*,

1381*s*, 1333*m*, 1270*s*, 1251*s*, 1171*m*, 1138*m*, 1110*s*, 1034*m*, 923*m*, 857*m*, 825*m*, 781*m*, 762*m*, 737*s*, 647*w*, 571*w*, 510*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 13.81 (br. *s*, 2 OH); 7.62 (*s*, 2 N=C−H); 7.30–7.19 (*m*, 6 arom. H); 6.89 (*dd*, $^3J = 7.7$, $^4J = 1.8$, 2 arom. H), 6.70 (*t*, $^3J = 7.6$, 2 arom. H); 6.65 (*dd*, $^3J = 7.7$, $^4J = 1.9$, 2 arom. H); 4.54 (*sept*. $^3J = 6.1$, 2 Me_2CHO); 4.29, 4.15 (*AB*, $J_{AB} = 14.0$, 2 CH_2N); 1.87 (*s*, 2 Me); 1.35, 1.34 (2*d*, $^3J = 6.1$, 2 Me_2CHO). ^{13}C-NMR (75 MHz, $CDCl_3$): 165.6 (CH=N); 152.9; 146.2; 137.4; 136.1; 135.2; 129.5; 128.0; 127.8; 126.7; 123.7; 119.0; 117.7; 71.4 (Me_2CHO); 61.4 (CH_2N); 22.1, 22.0 (Me_2CHO); 19.7 (Me).

4. *Co^{II} Complexes: General Procedure.* The ligand **3** (1 mmol) in EtOH (30 ml) was deprotonated with 2M KOH/MeOH (3 ml). To the yellow soln., $[Co^{II}(AcO)_2] \cdot 4\,H_2O$ (*Fluka*, 1 mmol equiv.) was added. The dark red soln. was stirred under N_2 at r.t. for 1 h, and then evaporated. The residue was extracted with $CHCl_3$ (5×50 ml), the collected org. phase dried (Na_2SO_4) and evaporated, and the brown powder crystallized (toluene or CH_2Cl_2/hexane): Co^{II} complex[Co^{II}(**3′**)].

The elemental analysis of Co^{II} complexes with alkoxy-substituted ligands indicated the presence of H_2O. Even after drying under high vacuum, followed immediately by analysis, H_2O was present. A series of successive analyses revealed the uptake of H_2O, even when the samples were stored under N_2.

*{(*M*)-*N,N′*-Bis[[2-(hydroxy-*κ*O)phenyl]methylidene}-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanaminato(2−)-*κ*N,*κ*N′}cobalt* ([Co^{II}(**3′a**)]): M.p. 175° (CH_2Cl_2/hexane). IR (KBr): 3017*m*, 2918*m*, 1609*s*, 1534*s*, 1465*s*, 1445*s*, 1397*m*, 1348*s*, 1319*s*, 1248*w*, 1190*m*, 1147*s*, 1128*m*, 1055*m*, 1030*m*, 970*w*, 908*m*, 849*w*, 798*m*, 752*s*, 679*w*, 612*w*, 588*w*, 512*w*, 465*w*. EI-MS: 505 (100), 399 (12), 372 (19), 370 (17), 191 (58), 178 (23). FAB-MS: 506 ([*M* + 1]). HR-FAB-MS: 506.1399 ($C_{30}H_{27}CoN_2O_2^+$; calc. 506.1404). Anal. calc. for $C_{30}H_{26}CoN_2O_2$ (505.49): C 71.28, H 5.18, N 5.54; found: C 71.05, H 5.11, N 5.49.

*{(*M*)-*N,N′*-Bis{[2-(hydroxy-*κ*O)-3-methoxyphenyl]methylidene}-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanaminato(2-)-*κ*N,*κ*N′}cobalt* ([Co^{II}(**3′b**)]): M.p. 165° (CH_2Cl_2/hexane). IR (KBr): 3441*m*, 3052*m*, 2922*m*, 2828*m*, 1603*s*, 1543*s*, 1467*s*, 1438*s*, 1400*s*, 1318*s*, 1244*s*, 1214*s*, 1168*m*, 1110*m*, 1082*m*, 1049*m*, 981*m*, 865*m*, 807*w*, 779*m*, 737*s*, 660*w*, 623*w*, 566*w*. ESI-MS: 565.2. Anal. calc. for $C_{32}H_{30}CoN_2O_4 \cdot (H_2O)_{0.5}$ (570.04): C 67.43, H 5.39, N 4.91; found: C 67.21, H 5.42, N 4.83.

*{(*P*)-*N,N′*-Bis{[5-bromo-2-(hydroxy-*κ*O)-3-methoxyphenyl]methylidene}-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanaminato(2-)-*κ*N,*κ*N′}cobalt* ([Co^{II}(**3′c**)]): M.p. 197° (CH_2Cl_2/hexane). IR (KBr): 3447*m*, 2928*m*, 1621*s*, 1540*s*, 1464*s*, 1316*s*, 1238*s*, 1212*s*, 1100*m*, 1050*s*, 985*w*, 874*m*, 839*m*, 791*m*, 758*s*, 701*m*, 662*w*, 620*w*, 568*m*, 540*w*, 527*w*, 514*w*, 502*w* , 487*w*, 474*w*. ESI-MS: 723.1.

*{(*M*)-*N,N′*-Bis{[2-(hydroxy-*κ*O)-3-hydroxyphenyl]methylidene}-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanaminato(2−)-*κ*N,*κ*N′}cobalt* ([Co^{II}(**3′g**)]): M.p. 197° (CH_2Cl_2/hexane). IR (KBr): 3401*w*, 3059*w*, 2928*m*, 1618*s*, 1554*m*, 1447*s*, 1403*m*, 1317*m*, 1264*s*, 1235*s*, 1095*m*, 1035*s*, 858*m*, 778*m*, 734*s*, 668*w*, 472*w*. ESI-MS: 537.5.

*{(*M*)-*N,N′*-Bis{[3-ethoxy-2-(hydroxy-*κ*O)phenyl]methylidene}-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanaminato(2−)-*κ*N,*κ*N′}cobalt* ([Co^{II}(**3′h**)]): M.p. 172° (CH_2Cl_2/hexane). IR (KBr): 3446*w*, 2974*m*, 2923*m*, 1608*s*, 1541*s*, 1466*s*, 1438*s*, 1395*s*, 1316*s*, 1239*s*, 1212*s*, 1175*m*, 1093*m*, 1048*m*, 901*m*, 858*m*, 806*w*, 779*m*, 737*s*, 650*w*, 457*w*. ESI-MS: 593.1. Anal. calc. for $C_{34}H_{34}CoN_2O_4 \cdot (H_2O)_{0.5}$ (593.59): C 68.28, H 5.81, N 4.68; found: C 67.99, H 5.90, N 4.54.

*{(*P*)-*N,N′*-Bis{[2-(hydroxy-*κ*O)-3-propoxyphenyl]methylidene}-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanaminato(2−)-*κ*N,*κ*N′}cobalt* ([Co^{II}(**3′i**)]): M.p. 178° (CH_2Cl_2/hexane). IR (KBr): 3452*w*, 2961*m*, 2870*m*, 1602*s*, 1544*m*, 1463*s*, 1439*s*, 1402*m*, 1317*m*, 1240*m*, 1211*s*, 1082*w*, 1055*m*, 958*w*, 861*m*, 778*m*, 736*s*, 649*w*, 509*w*. ESI-MS: 621.3.

*{(*M*)-*N,N′*-Bis{[2-(hydroxy-*κ*O)-3-(phenylmethoxy)phenyl]methylidene}-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanaminato(2-)-*κ*N,*κ*N′}cobalt* ([Co^{II}(**3′k**)]): M.p. 192° (CH_2Cl_2/hexane). IR (KBr): 3445*w*, 3028*w*, 2892*m*, 1603*s*, 1542*m*, 1496*w*, 1438*s*, 1401*m*, 1316*m*, 1212*s*, 1171*m*, 1087*w*, 1049*m*, 980*w*, 861*m*, 807*w*, 778*m*, 736*s*, 696*m*, 668*w*, 649*w*, 618*w*, 507*w*. ESI-MS: 713.4.

*{(*P*)-*N,N′*-Bis{[2-(hydroxy-*κ*O)-3-(2-methylpropoxy)phenyl]methylidene}-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanaminato(2-)-*κ*N,*κ*N′}cobalt* ([Co^{II}(**3′l**)]): M.p. 182° (CH_2Cl_2/hexane). IR (KBr): 3445*w*, 3053*m*, 2955*m*, 2870*m*, 1603*s*, 1543*m*, 1463*s*, 1437*s*, 1401*m*, 1318*m*, 1242*s*, 1211*s*, 1175*m*, 1080*m*, 1045*m*, 862*m*, 779*m*, 737*s*, 650*w*, 512*w*, 448*w*. ESI-MS: 649.3.

*{(*M*)-*N,N′*-Bis{[2-(hydroxy-*κ*O)-3-(1-methylethoxy)phenyl]methylidene}-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanaminato(2-)-*κ*N,*κ*N′}cobalt* ([Co^{II}(**3′m**)]): M.p. 172° (CH_2Cl_2/hexane). IR (KBr): 3445*w*, 3055*w*, 2959*m*, 2875*m*, 1604*s*, 1545*m*, 1464*s*, 1440*s*, 1401*m*, 1317*m*, 1241*s*, 1211*s*, 1079*m*, 1052*m*, 863*m*, 779*m*, 737*s*, 648*w*, 510*w*. ESI-MS: 621.3.

Complexes [Mn^{II}(**3′b**)], [Fe^{II}(**3′b**)], [Ni^{II}(**3′b**)], and [Cu^{II}(**3′b**)] were synthesized similarly to the Co^{II} complexes.

*{(*P*)-*N,N′*-Bis[[2-(hydroxy-*κ*O)-3-methoxyphenyl]methylidene}-6,6′-dimethyl[1,1′-biphenyl]-2,2′-dimethanaminato(2−)-*κ*N,*κ*N′}zinc* ([Zn(**3′b**)]) was synthesized by addition of $ZnEt_2$ (0.2 mmol; previously evaporated from 1.0M $ZnEt_2$ soln. in hexane), in (D_6)benzene to **3b** (0.2 mmol) in (D_6)benzene (2 ml). ^{1}H-NMR (300 MHz, C_6D_6): 6.90–6.85 (*m*, 4 arom. H); 6.84 (*s*, 2 N=C−H); 6.63 (*t*, ^3J = 7.4); 6.58 (*dd*, ^3J = 7.4, ^4J = 1.4); 6.48 (*t*, ^3J = 7.8); 6.30 (*dd*, ^3J = 8.0, ^4J = 1.7); 4.04 (*Ad*, J_{AB} = 14.7, ^4J = 1.4, 2 H, 2 CH_2N); 3.67 (*s*, 2 MeO); 3.53 (*Bd*, J_{AB} = 14.8, 2 H, 2 CH_2N); 1.71 (*s*, 2 Me).

5. *Ethylation of Aldehydes with Various Transition-Metal Catalysts: General Procedure.* 5.1. *For $AlClEt_2$, $Ti(i\text{-}PrO)_4$, and $ZnEt_2$.* Under N_2 and r.t., the ligand **3a–f** (0.05 mmol) was dissolved in toluene (2 ml). To the yellow soln., the basic Al, Ti, Zn complex (0.05 mmol) was added, and stirring was continued for 1 h. Then, $ZnEt_2$ (1 mmol) was added, followed, after 5 min, by benzaldehyde (0.5 mmol). The soln. was stirred for 18 h at r.t. and then analyzed by HPLC and ^{1}H-NMR. Results: see *Fig. 1* and *Table 1*.

5.2. *Complexes [Co^{II}(**3′a–m**)], [Mn^{II}(**3′b**)], [Fe^{II}(**3′b**)], [Ni^{II}(**3′b**)], or [Cu^{II}(**3′b**)].* The corresponding complex (0.05 mmol) was dissolved in toluene (2 ml). $ZnEt_2$ (1 mmol) was added in one portion to the colored soln. After 5 min, the aldehyde was added as described in *Exper. 5.1*. The mixture was stirred at r.t., and then the conversion (mesitylene as internal standard) and the stereochemical outcome were analyzed by HPLC and ^{1}H-NMR or GC. Results: see *Fig. 1* and *Tables 2–4*.

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