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C_2 and C_1 Symmetry of chiral auxiliaries in catalytic reactions on metal complexes

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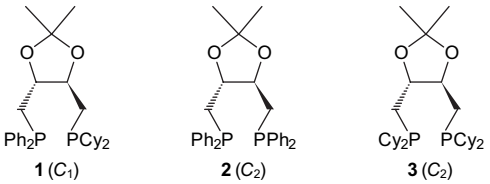
1. Introduction

At present, considerable experimental data are available to answer the question put formerly:[1] are chiral auxiliaries with a C_2 symmetry axis (C_2-symmetric) or C_1-symmetric chiral (asymmetric) auxiliaries best suited in principle for maximal reaction enantioselectivity? It is believed[1] that 'auxiliaries with C_2 symmetry elements perform as stereochemical directors to provide higher levels of absolute stereochemical control, as compared to those totally lacking symmetry'. Indeed, many asymmetric reactions are very successful using C_2-symmetric chiral auxiliaries (see, for example, a recent review in Ref. 2). However, there are some reactions,[3,4] which contradict this postulate. Indeed, 'there is no fundamental reason why a C_2-symmetric ligand should necessarily be superior to a non-symmetric counterpart. In fact, for certain reactions, good arguments can be found which suggest that non-symmetrical ligands with two different coordinating heteroatoms could allow more effective enantiocontrol than C_2-symmetric ligands'.[4] A lack of catalyst symmetry can be helpful for enantioselectivity of some reactions. For example, C_1-(*R*,*R*)-DIOCP (**1**) is more effective than C_2-(*R*,*R*)-DIOP (**2**) and C_2-(*R*,*R*)-Cy-DIOP (**3**) in the asymmetric hydrogenation of ketopantoyllactone on Rh complexes (ee=72–75(*R*), 37–52(*R*), 45(*R*), correspondingly)[5] in similar reaction conditions.



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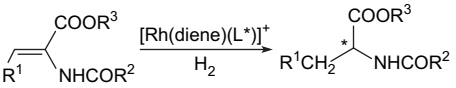
In this paper, an effort has been made to compare C_2- and C_1-ligand effectiveness in some asymmetric reactions on metal complexes using a single substrate and the same metal atom within a reaction in similar reaction conditions. For example, enantioselectivities of reactions in the presence of complexes with C_2-diols, C_2-diamines and C_1-amino alcohols or C_2-diamines and *N*-substituted C_1-diamines with a similar chiral array have been compared. In these reactions, structural and electronic effects do not prevail over the symmetry parameters. However, this approach fails sometimes, because the structures of C_2- and C_1-ligands differ significantly. Thus, in these cases, the comparison has been made formally. The maximal values of ee of a product were compared between reactions over C_2 and C_1 chiral auxiliaries very dissimilar in structure. It has been noted recently[6] that important intermediates of very enantioselective reactions on complexes with C_2-ligands are non-symmetric (asymmetric). Reactions with different enantioselectivity levels depending on the C_2 or C_1 symmetry of the chiral auxiliaries are discussed in this paper. It should be emphasized that reactions of this type are observed only for monofunctionalized substrates. Thus, these reactions are outlined in the review in the following sequence of the simplest (mainly aromatic) substrates used: aldehyde, ketone and unfunctionalized olefins.

The next section will briefly review the most studied reactions with very high enantioselectivity values, which do not depend on C_2 or C_1 symmetry of chiral auxiliaries.

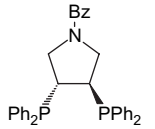
2. Catalytic asymmetric reactions indifferent to C_2–C_1 symmetry of chiral auxiliaries

The most efficient ligands **4**–**20** of Rh complexes in the hydrogenation of amino acid precursors 1 with an enantiomeric excess (ee) of the products are presented below:[7–20]

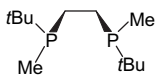


(1)

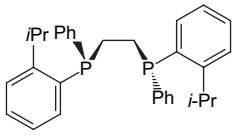
R^1=H, R^2=Me, R^3=Me AcAlaOMe
R^1=Ph, R^2=Me, R^3=H AcPhe
R^1=Ph, R^2=Ph, R^3=H BzPhe
R^1=Ph, R^2=Me, R^3=Me AcPheOMe.



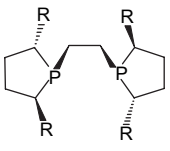
4, 99 (S)(AcPhe)[7]



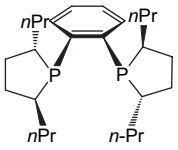
5, 98.4 (R)(AcPhe)[8a,b]
99.9 (R)(AcPheOMe)[8a,b]



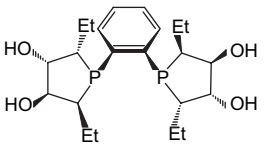
6, >99(R)(AcPheOMe)[9]



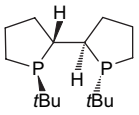
7: R=Et, 98(*S*)(AcAlaOMe)[10]
8: R=Ph, 99(*S*)(AcPheOMe)[11]



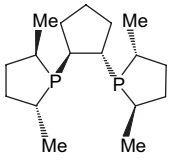
9, 99.8(*S*)(AcPheOMe)[10]



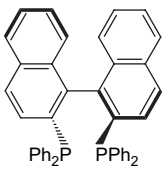
10, >99(*S*)(AcPhe)[12]



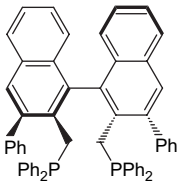
11, >99(*R*)(AcPhe)[13]



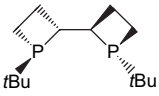
12, >98(*R*)(AcPheOMe)[14]



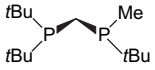
(*R*)-**13**, 100(*S*)(BzPhe)[15a]
(*S*)-**13**, 98(*R*)(BzPhe)[15b]



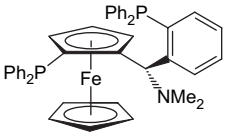
14, 97.8 (*R*)(AcPhe)[16]



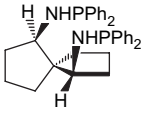
15, > 99(*R*)(AcPheOMe)[8c]



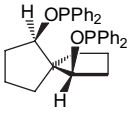
16, > 99(*R*)(AcPhe)[17]



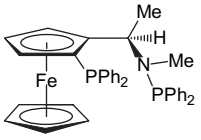
17, > 99(*conf. is not indicated*)(AcAlaOMe)[18]



18, > 99(*R*)(AcPheOMe)[19a]

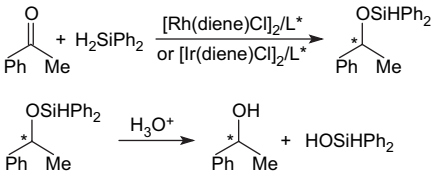


19, 97.9 (*R*)(AcPhe)[19b]



20, > 99.4(*S*)(AcPhe)[20]

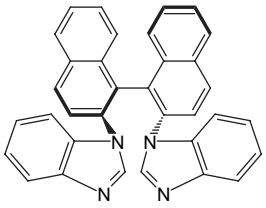
It can be seen that the maximal enantiomeric excess (ee) of reaction 1 products falls within the range from 98 to 100% ee independently of Rh complexes with C_2-symmetric (**4**–**15**) or C_1-symmetric (**16**–**20**) ligands as catalysts. A similar situation is found in the hydrosilylation of acetophenone by diphenylsilane on rhodium and iridium complexes:[21,22]



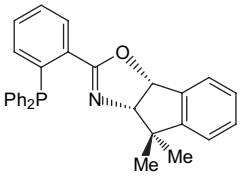
(2)

The maximal enantioselectivity of reaction 2 on Rh and Ir complexes with ligands **21**–**23** lies in the interval of 94–98% ee irrespective of ligand symmetry. Along with the hydrogenation

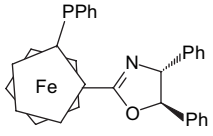
L*=



21, Rh, 98 (*R*)[21a]

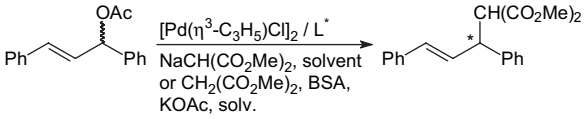


22, Rh, 94(*R*)[21b]



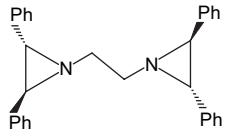
23, Ir, 96(*R*)[22]

reaction 1, an allylic alkylation reaction 3 on chiral palladium complexes is another well-studied asymmetric reaction:[6a,23]

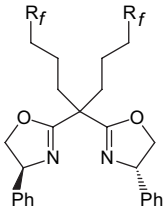


(3)

This reaction proceeds with maximal ee values on palladium complexes with ligands **24**–**28**.[24–27]

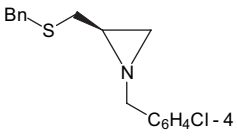


24, >99(*S*)[24]

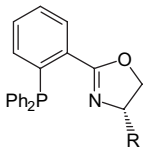


$R_f = C_{10}F_{21}$

25, 98(*S*)[25]



26, 99(*S*)[26]

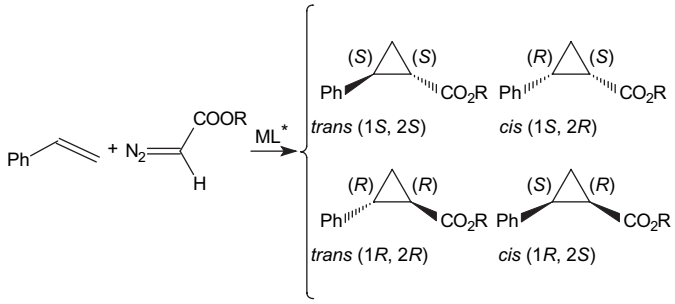


27: R=*i*-Pr, 99(*S*),[27a] 98(*S*),[27b] 98.5(*S*),[27c]
28: R=Ph, 99(*S*),[27b]

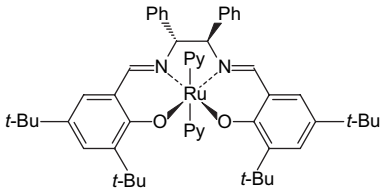
The degrees of enantioselectivity using C_2(**24**,**25**)- and C_1(**26**–**28**)-symmetric ligands in reaction 3 also do not differ.

A study of styrene cyclopropanation with diazoacetate esters[28] includes a very wide range of C_2-symmetric ligands.

The maximal enantioselectivity[†] is only specific for a complex with C_2-symmetric ligands **29**.[29]



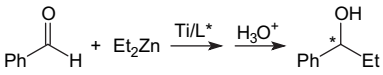
(4)



RuPy$_2$(**29**): R=Et, >99 *trans*(1*R*,2*R*), >99 *cis*(1*R*,2*S*) (*trans*:*cis* = 3.4:1)[29]

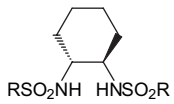
C_1-Symmetric complexes are less well studied in this reaction (maximal ee values 93 *cis*(1*S*,2*R*)[28b] and 98 *cis*(1*S*,2*R*)[30]).

A well-studied reaction is diethylzinc addition to benzaldehyde catalyzed by titanium complexes:[31]

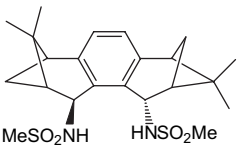


(5)

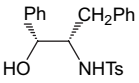
As in the case of reactions 1–4, the maximal enantioselectivity of reaction 5 for complexes with C_2 (**30**,**31**)- and C_1 (**32**–**34**)-symmetric ligands is actually equal.[32–36]



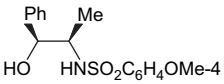
30: R = C_6H_4OMe-4, 98(*S*)[32]
31: R = CF_3, 99(*S*)[33]



-**32**, 98(*R*)[34]

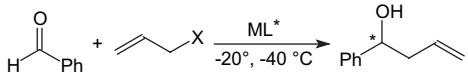


33, > 99(*R*)[35]



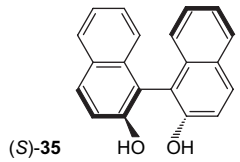
34, 97(*S*)[36]

A highly enantioselective and well-studied reaction is aldehyde allylation on C_2 chiral Lewis acids with ligands **10** and **35** as catalysts:[37]



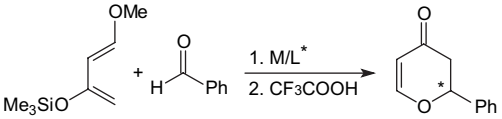
X=Si(OMe)$_3$ (6); X=SnBu$_3$ (7)

[†] Because the relationship between enantiomeric *trans*(1*S*,2*S*) and *trans*(1*R*,2*R*) as well as enantiomeric *cis*(1*S*,2*R*) and *cis*(1*R*,2*S*) products of reaction 4 is determined chromatographically, using a chiral column, ee values and trans:cis ratios are accepted to be an indication of enantioselectivity.



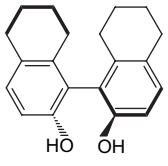
Reaction	ML*	ee (conf.)
6	AgF·(*R*)-**10**	94(*R*)[38a]
7	AgOTf·(*S*)-**10**	96(*S*)[38b]
7	Ti(O-*i*-Pr)$_4$/(*R*)-**35**/MS 4 Å	96(*R*)[39]
7	$TiCl_2$·(*S*)-**35**/MS 4 Å	97(*S*)[40]
7	Bis-[Ti(O-*i*-Pr)·(*S*)-**35**]oxide	96(*S*)[41]
7	$InCl_3$/(*S*)-**35**/MS 4 Å	92(*S*)[42]
7	Zr(O-*i*-Pr)$_2$·(*S*)-**35**/MS 4 Å	93(*S*)[43]

Finally, a good example for comparing the enantioselective action of C_2- and C_1-symmetric chiral complexes—the Diels–Alder reaction of Danishefsky's dienes and benzaldehyde,[44] is shown in reaction 8.

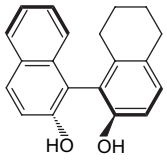


(8)

No appreciable changes in enantioselectivity are observed in a series of titanium complexes with C_2(**36**)- and C_1(**37**)-ligands of analogous structure acting as catalysts in reaction 8.[45,46]



36, 97(*R*),[45] 99.4 (*R*)[46]



37, 95(*R*),[45] 99.3 (*R*)[46]

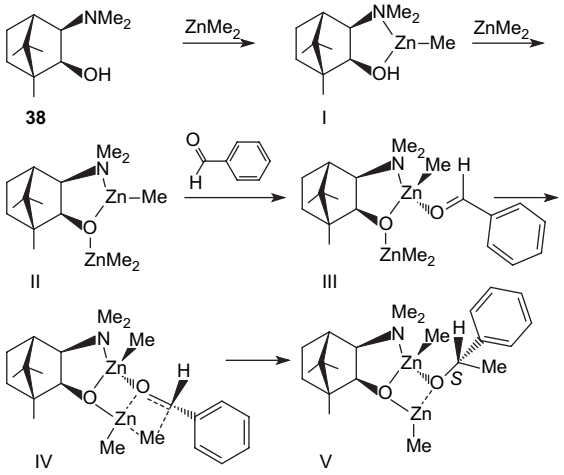
In line with two alternative mechanisms of reaction 1[6a,b] and mechanisms of reactions 2,[6b] 3,[6a] 4,[47] 5,[33,48] 6,[37] 7,[37,38] 8,[45,49] the starting C_2-symmetric complexes lose C_2 symmetry prior to the asymmetric induction stage.

All of the above data are in favour of the view that the C_2 and C_1 chiral auxiliaries do not differ in their maximal enantioselective action within the reactions listed above and many others.

3. Addition of diethylzinc to benzaldehyde in the presence of amino alcohols and related compounds

Chiral amino alcohols, amido alcohols, diamines, diols, amino thiols, disulfides and diselenides form part of an in situ catalytic system in the asymmetric alkylation of aldehydes by dialkylzinc.[31] A standard reaction in this case is also reaction 5, although without Ti(O-*i*-Pr)$_4$ as a catalytic complex-forming particle.

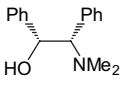
Experimental and theoretical studies of the mechanism of benzaldehyde and dialkylzinc interaction in the presence of chiral amino alcohols of the type **38** allow the understanding of the reaction-step sequence in this reaction[31,50–54] (Scheme 1).



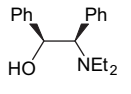
Scheme 1.

In the first stage, a chelate complex of zinc with the amino alcohol (intermediate II) is formed, which is a catalyst of the reaction.

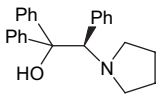
A basic feature of all chiral compounds used as ligands in this reaction is the C_1 symmetry (asymmetry). The ligands **39**–**60** taking part in the most enantioselective reactions are listed below with ee values of the product (1-phenylpropanol):[55–78]



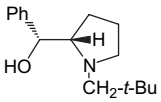
39, 97(*R*)[55]



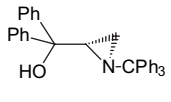
40, 94(*S*)[56]



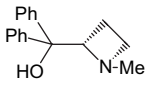
41, 97(*S*)[57]



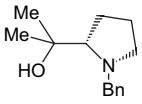
42, 100(*R*)[58]



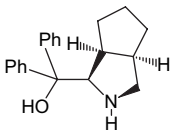
43, 99(*S*)[59,60]



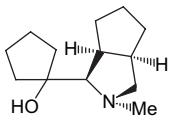
44, 98(*S*)[61]



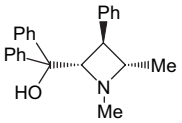
45, 99(*R*)[62]



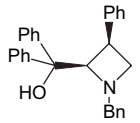
46, 99(*R*)[63–68]



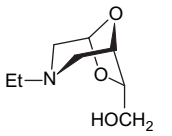
47, 99(*R*)[63–73]



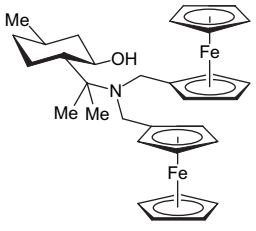
48, 98(*S*)[69]



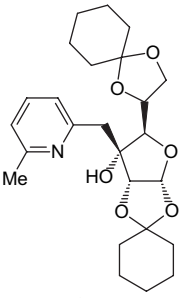
49, 98(*R*)[69]



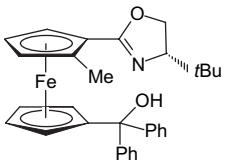
50, 94(*S*)[70]



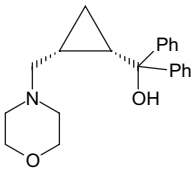
51, 95(*S*)[71]



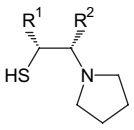
52, 92(*S*)[72]



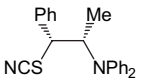
53, 95(*R*)[73]



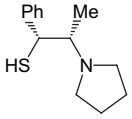
54, 96(*R*)[74]



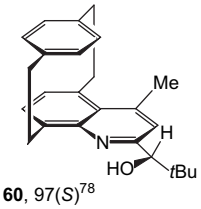
55: $R^1 = R^2 =$ Ph, 99.3(*R*)[75]
56: $R^1 = R^2 =$ *i*-Pr, 99.6(*R*)[75]
57: $R^1 =$ *i*-Pr, $R^2 =$ Ph, 99.5(*R*)[75]



58, 96(*R*)[76]

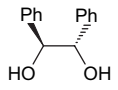


59, 100(*R*)[77]

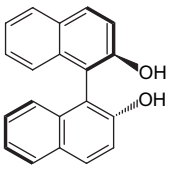


60, 97(*S*)[78]

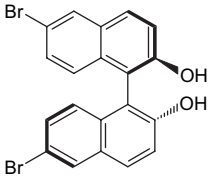
Far lower ee values of the product (1-phenylpropanol) are found in the reactions with C_2-symmetric diols **35**, **61**–**63**, diamine **65** and diimine **64**:[79,80]



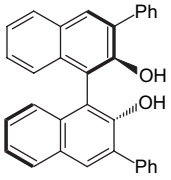
61, 20(*R*)[79]



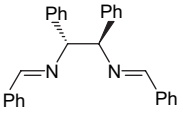
(R)-35,8(*S*)[79]



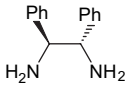
62, 10(*R*)[79]



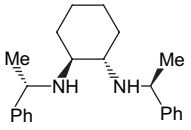
63, 40(*R*)[79]



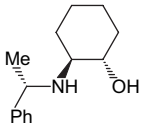
64, 1(*S*)[79]



65, 20(*S*)[79]



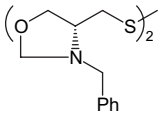
66, 3(*S*)[80]



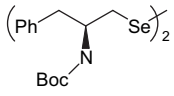
67, 57(*R*)[80]

C_1-Amino alcohol **67** gives a far better enantioselectivity in comparison with C_2-diamine **66**. There are a few tetradentate C_2-symmetric ligands, which participate in the reaction with high enantioselectivity (Table 1).

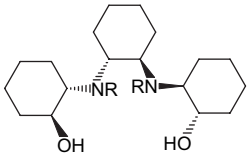
As apparent from Table 1, reaction 5 (without Ti(O-*i*-Pr)$_4$) on tetradentate 'dimeric' ligands **69**, **71**, **73**, **75**, **77**, **79**, **80**, **82**, **84**, **86**, **88** and **90** occurs with practically complete coincidence of the product ee values (configuration), as in the case of corresponding 'monomeric' C_1-symmetric ligands **68**, **70**, **72**, **74**, **76**, **78**, **46**, **81**, **83**, **85**, **87** and **89**. This agreement is unlikely to be accidental. It is assumed that the tetradentate C_2-symmetric ligands are most probably involved in the reaction by their bidentate C_1-symmetric (asymmetric) fragments. Furthermore, active catalysts of the reaction on disulfides **84**, **86**, **88**, **90** and **91** are most likely to be the corresponding ethylzinc thiolate produced from the disulfide cleavage by diethylzinc, as described earlier.[96] The same cleavage may also occur in the reaction over diselenide **92**. A few C_2-symmetric tetradentate ligands, for example, **93** and **94**, in this reaction have not been included in Table 1, due to a lack of pertinent information on the 'monomeric' C_1-symmetric bidentate ligands.[94,95,97,98]



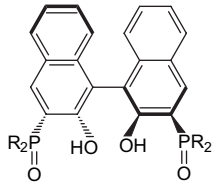
91, >99(*S*)[94]



92, 96(*R*)[95]



93: R=H, 80(*R*)[97]
94: R=Me, 92(*S*)[97]



95: R=Ph, 95(*R*)[98a]
96: R=NMe_2, 97(*R*)[98b]

There is reason to believe that asymmetric induction in reaction 5 without Ti(O-*i*-Pr)$_4$ takes place in the transition state on the basis of the C_1-bidentate fragment of C_2-tetradentate ligands **95** and **96**.[98]

There is experimental evidence that the ligand C_1-bidentate fragment is involved in the reaction in the case of C_2-symmetric tridentate ligands **97**, **99**, **101** and **103** (Table 2).

A similarity of the enantioselectivity values in reaction 5 without Ti(O-*i*-Pr)$_4$ in the case of these ligands and their C_1-symmetric (asymmetric) bidentate fragments in the corresponding ligands **98**, **100**, **102** and **104** adds to this conclusion. Some divergence in the product ee values is observed only with ligands **97** and **98** (Table 2, Entry 1). On the other hand, the reaction in the presence of chiral C_2-symmetric bidentate ligands proceeds with low enantioselectivity, negligibly small in the case of ligands of the type **105**–**108** (Table 3). To raise the product ee values, addition of Ti(O-*i*-Pr)$_4$ to the catalytic system is necessary.

This Ti(O-*i*-Pr)$_4$ addition serves as the basis of a stereomechanism of the reaction[104,105] different from that without Ti(O-*i*-Pr)$_4$. The results of diethylzinc addition to benzaldehyde in the presence of chiral ligands **109**–**114** with the C_2 symmetry axis passing through the donor nitrogen atom are presented below.[105–108]

As seen from the ee values, the ability of an oxygen atom in the C_2-symmetric cyclic fragment of ligands **112**–**114** to be coordinated by the zinc atom in the intermediate complex, as compared to ligands **109** and **110**, correlates with a positive dramatic rise of the ee values of the reaction product. The

Table 1
Addition of diethylzinc to benzaldehyde in the presence of 'monomeric' chiral C_1-symmetric and 'dimeric' chiral C_2-symmetric ligands (toluene, rt)

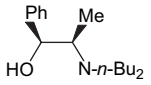
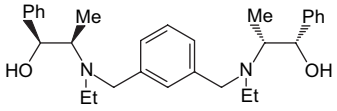
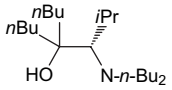
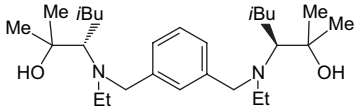
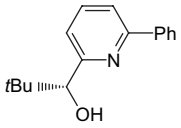
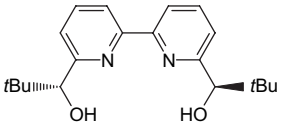
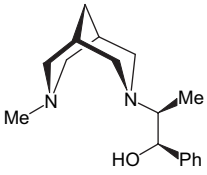
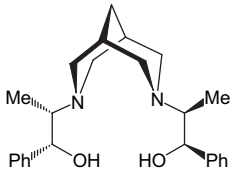
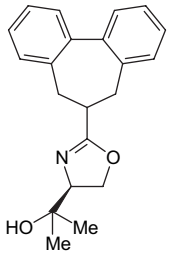
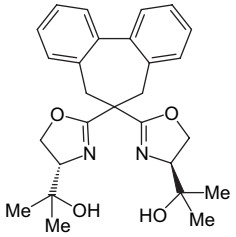
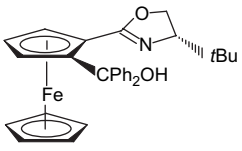
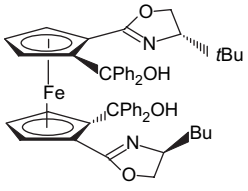
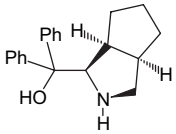
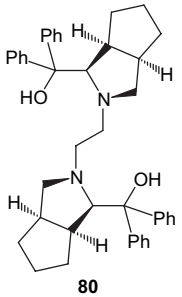
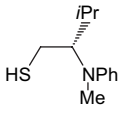
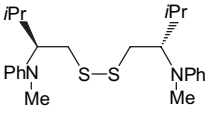
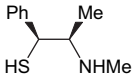
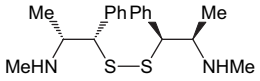
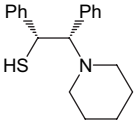
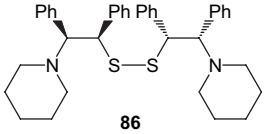
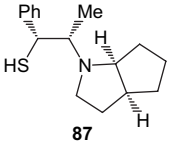
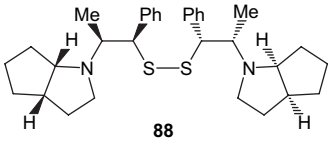
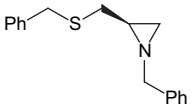
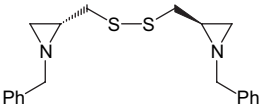
Entry	'Monomeric' ligand	ee [%] (config. of product)	'Dimeric' ligand	ee [%] (config. of product)
1	 **68**	90(*S*)[81]	 **69**	93(*S*)[82]
2	 **70**	97(*R*)[83]	 **71**	96(*R*)[82]
3	 **72**	90–93(*R*)[84]	 **73**	93(*R*)[84]
4	 **74**	98(*R*)[85]	 **75**	85(*R*)[85]
5	 **76**	61(*R*)[86]	 **77**	65–87(*R*)[86]
6	 **78**	93(*R*)[87]	 **79**	91(*R*)[88]
7	 **46**	99(*R*)[63]	 **80**	100(*R*)[63]
8	 **81**	82(*R*)[89]	 **82**	80(*R*)[89]

Table 1 (*continued*)

Entry	'Monomeric' ligand	ee [%] (config. of product)	'Dimeric' ligand	ee [%] (config. of product)
9	 **83**	80(*R*)[90]	 **84**	86(*R*)[90]
10	 **85**	99(*R*)[91]	 **86**	99(*R*)[91]
11	 **87**	90(*R*)[92]	 **88**	86(*R*)[92]
12	 **89**	76(*S*)[93]	 **90**	87–99(*S*)[93]

same ability of ligands **109** and **110** is less profound, because the volume of the groups around the oxygen atom prevents the coordination. A molecular model analysis of the above ligands shows that the coordination of ligand donor atoms and the oxygen atom of one of the C_2-symmetric disposed groups in the *N*-containing cycle is sterically possible. As a result, the oxygen atom of another group appears to be out of the coordination reach. This leads to a loss of C_2 symmetry in these ligands after the coordination in a catalytic complex. Therefore, a positive boost of enantioselectivity values in this case may be explained by a decline of symmetry of the important intermediate complex, due to the additional coordination of the

Table 2
Addition of diethylzinc to benzaldehyde in the presence of chiral C_2-symmetric tridentate ligands and their asymmetric analogues (hexane, rt)[99]

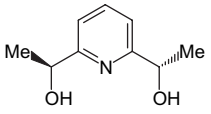
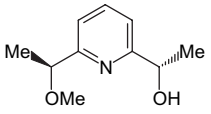
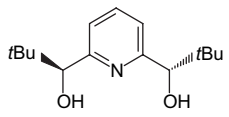
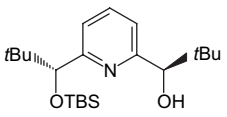
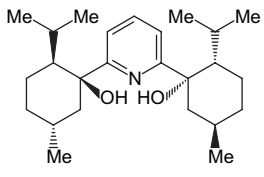
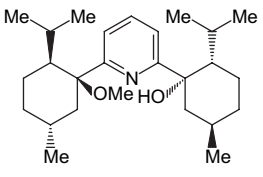
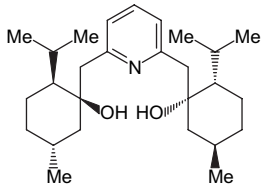
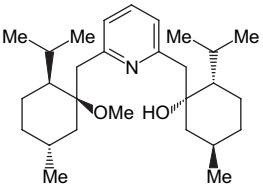
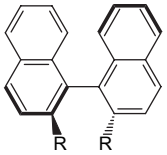
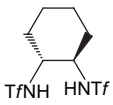
Entry	Chiral C_2-symmetric ligand	ee [%] (config. of product)	Asymmetric ligand	ee [%] (config. of product)
1	 **97**	4(*S*)	 **98**	47(*S*)
2	 **99**	65(*S*)	 **100**	67(*R*)
3	 **101**	55(*S*)	 **102**	35(*S*)
4	 **103**	93(*S*)	 **104**	95(*S*)

Table 3
Addition of diethylzinc to benzaldehyde in the presence of chiral C_2-symmetric ligands with and without Ti(O-*i*-Pr)$_4$

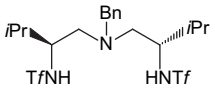
Entry	Catalytic system PhCHO/Et_2Zn/ligand	ee [%] (config. of product)	Ref.	Catalytic system PhCHO/Et_2Zn/ligand/Ti(O-*i*-Pr)$_4$	ee [%] (config. of product)	Ref.
1	(*S*)-**35**	No reaction	100	(*S*)-**35**	92(*S*)	100
2	**105**	8(*R*)	101	—	—	
3	**106**	54(*S*)	33, 102	**106**	99(*S*)	33, 102
4[a]	**107**	15(*S*)	103	**107**	72(*S*)	103
5[b,c]	**108**	15	104	—	—	—
6[d]	**108**	0	105	—	—	—



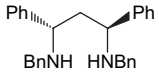
(*S*)-**35**: R = OH
105: R = NMePh



106

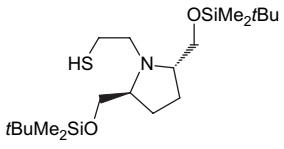


107

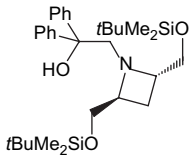


108

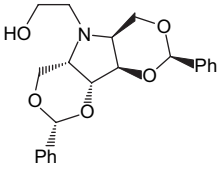
[a] In the presence of MS 4 Å.
[b] *p*-$CF_3C_6H_4CHO$.
[c] Configuration of product not indicated.
[d] *p*-MeC_6H_4CHO.



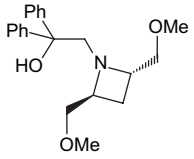
109, 9(*R*)[105a]



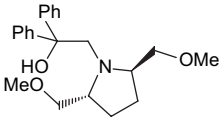
110, 20(*S*)[105b]



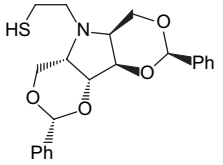
111, 42(*S*)[106,107]



112, 92(*S*)[105b]



113, 91(*R*)[108]



114, 96(S)[106,107]

oxygen atom of one of the C_2-symmetrically disposed groups of the ligands by the zinc atom.

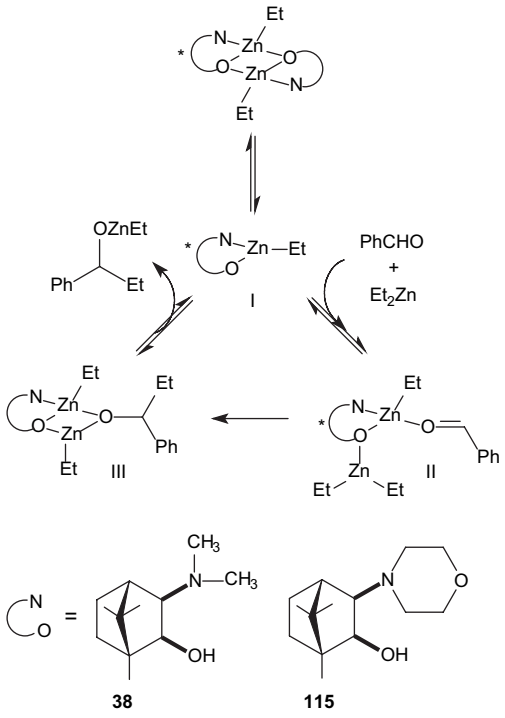
Thus, the complex with C_2-symmetric ligands of the related structure, being incapable of additional coordination, catalyzes the reaction with less enantioselectivity, because the intermediate complex responsible for asymmetric induction provides a higher symmetry of the elements than the C_1-axis.

The catalytic cycle has been proposed for reaction 5 without Ti(O-*i*-Pr)$_4$ in the presence of asymmetric ligands of the type **38** and **115**, based on a calorimetric study of the reaction kinetics[109] (Scheme 2).

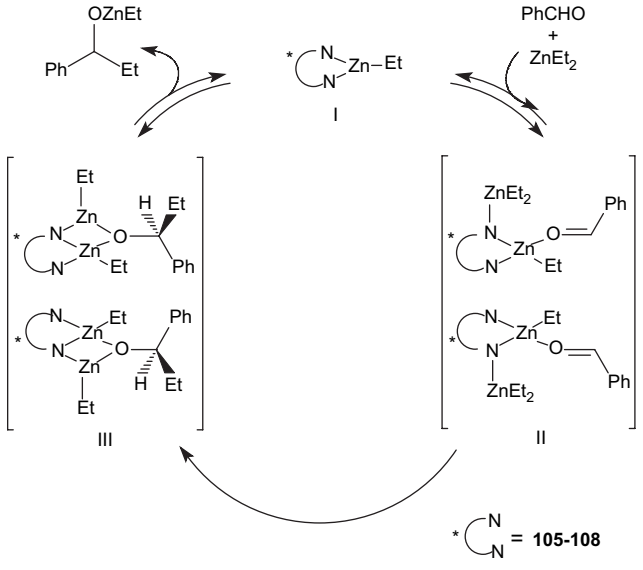
According to this scheme, the asymmetric induction will proceed during stage II→III. Extending mechanistically this model to the reaction in the presence of chiral C_2-symmetric ligands of the types **105**–**108** (Scheme 3), it may be assumed that the analogous stage II→III is also responsible for asymmetric induction. The key intermediate II that controls asymmetric induction could form in two variants (Scheme 3). These two molecules have very similar structures.

The configurations of $ZnEt_2$-*N* fragments of the left parts of these molecules are identical.[‡] The right parts are based on *proS*- and *proR*-coordinated benzaldehyde. Therefore, there is reason to believe that the free activation energies of formation of these molecules are very close in value. Hence, it can be assumed that they are formed in similar concentrations. As a result of the reaction stage II→III, the enantioselectivity is very low in this case. Thus, it is conceivable that the low enantioselectivity values of reaction 5 without Ti(O-*i*-Pr)$_4$ (Table 3) can be explained on the grounds of the above interpretation. Thus, diethylzinc addition to benzaldehyde in the presence of amino alcohols and related compounds without Ti(O-*i*-Pr)$_4$ occurs with high ee values of the product only for chiral C_1-symmetric (asymmetric) ligands. This reaction in the presence of chiral C_2-symmetric bidentate ligands, as a rule, proceeds with very low enantioselectivity values.

[‡] Absolute configurations of the *N*-substituted asymmetric nitrogen atoms in a metal complex of this ligand are the same according to calculations.[110]



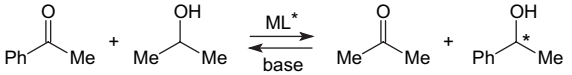
Scheme 2.



Scheme 3.

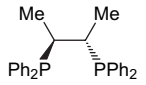
4. Hydrogen transfer hydrogenation of acetophenone in the presence of Rh, Ir and Ru complexes

Hydrogen transfer hydrogenation of prochiral ketones is one among the well-studied asymmetric reactions in the presence of chiral metal complexes.[111] Acetophenone is the most popular substrate in this reaction:



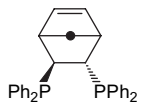
(9)

Extremely low ee values of the product have engaged our attention in reaction 9 on rhodium, iridium and ruthenium complexes with chiral C_2-symmetric bis(diphenyl)phosphine ligands **2**, **13** and **116**–**118**:[111,112a,112b,113]

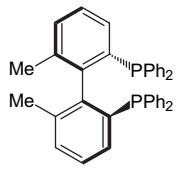


116, Rh, <1;[112a] Ir, 4–28(*S*)[112b] Ru, 1(*S*)–30(*R*)[111]

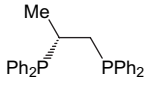
(*R*,*R*)-**2**, Rh, <1;[112a] Ru, 2(*R*)-8(*S*)[113]
(*R*)-**13**, Ru, 30(*S*)[113]



117, Ru, 28(*R*)[113]



118, Ru, 15(*R*)[113]



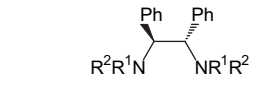
119, Ir, 4–58(*S*);[112b] Ru, 52(*S*)[113]

A modest ee value increase takes place in the case of a complex with asymmetric ligand **119**.

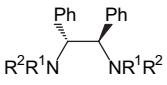
Table 4
Hydrogen transfer hydrogenation of acetophenone on Rh and Ir complexes with diamine, diimine and other bidentate ligands of C_2 and C_1 symmetry

Ligand	Symmetry	M	ee [%] (config. of 1-phenylethanol)	Ref.
65	C_2	Rh	17(*R*)	112
(*S*,*S*)-**120**	C_2	Rh	67(*R*)	112
121	C_2	Rh	28(*R*)	112
122	C_2	Rh	<10(*R*)	115
122	C_2	Ir	<10(*R*)	115
123	C_2	Rh	43(*R*)	116
(*R*,*R*)-**120**	C_2	Rh	63(*S*)	115
(*R*,*R*)-**120**	C_2	Ir	36(*S*)	115
124	C_2	Rh	37(*S*)	115
124	C_2	Ir	25(*S*)	115
125	C_2	Rh	65(*S*)	115
125	C_2	Ir	50(*S*)	115
(*R*,*R*)-**126**	C_2	Rh	12(*S*)	112c
127	C_2	Rh	0	112c
(*R*)-**128**	C_2	Rh	0	112c
129	C_2	Rh	32[a]	114
130	C_2	Ir	58(*R*)	117
131	C_2	Rh	48(*S*)	118
132	C_2	Rh	10(*R*)	119
133	C_2	Rh	32(*R*)	119
134	C_2	Rh	27(*R*)	119
(*S*,*S*)-**135**	C_1	Rh	90(*S*)	120
(*S*,*S*)-**135**	C_1	Ir	90(*S*)	120
(*R*,*R*)-**135**	C_1	Rh	90(*R*)	121, 122
(*R*,*R*)-**136**	C_1	Rh	97(*R*)	121
(*R*,*R*)-**136**	C_1	Ir	96(*R*)	121
137	C_1	Ir	82(*S*)	123
138	C_1	Ir	80(*R*)	123

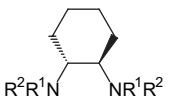
[a] Configuration not indicated.



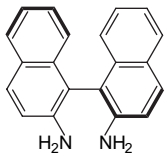
	R^1	R^2
(*S*,*S*)-**65**:	H	H
120:	H	Me
121:	H	*i*-Pr
122:	H	CSNHPh
123:	Me	CONHPh



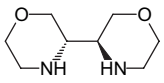
	R^1	R^2
(*R*,*R*)-**120**:	H	Me
124:	Me	CSNH-*n*-Pr
125:	Me	CSNHNp-1



	R^1	R^2
(*R*,*R*)-**126**:	H	H
127:	H	Me



(*R*)-**128**



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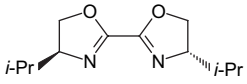

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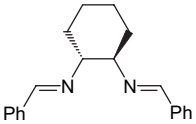
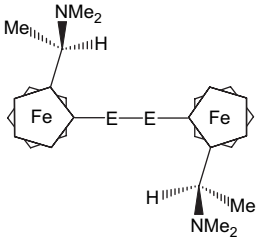
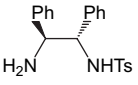


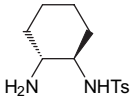
131



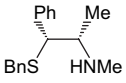
132: E = S
133: E = Se
134: E = Te



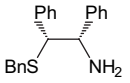
(*S*,*S*)-**135**



(*R*,*R*)-**136**



137

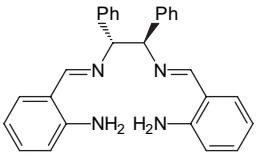


138

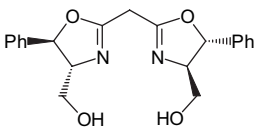
A quantitative leap in ee values occurs in the transition from chiral C_2-symmetric ligands **65** and **120**–**134** to chiral C_1-symmetric (asymmetric) ligands **135**–**138** in rhodium and iridium complexes of the [M(diene)Cl]$_2$/L* type as catalysts of hydrogen transfer hydrogenation of acetophenone (Table 4). Reaction 9 on C_2-symmetric Rh/(*R*)-2,2′-diamino-1,1′-binaphthalene (**128**) and Rh(**127**) complexes with ee=0%[112c] stays absolutely unexplained.

A similar situation occurs in the case of Rh and Ir complexes with C_2-symmetric tetradentate ligands **139**–**144**:[124–126]

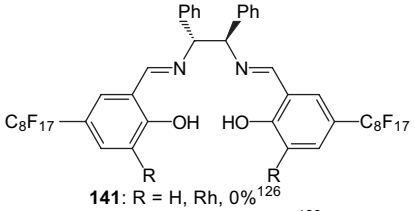
A similar quantitative leap in enantioselectivity of reaction 9 is found in the transition from chiral C_2- to C_1-symmetric bidentate ligands (complexes) **145**–**162** of ruthenium catalysts of the ‘in situ’ type (Table 5).



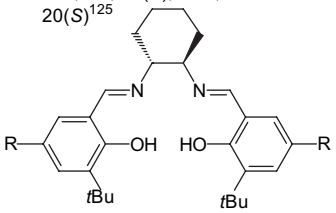
139,Rh, 0%;[124] Ir, 20(*S*)[124]



140, Rh, 16(*S*);[125] Ir, 20(*S*)[125]



141: R = H, Rh, 0%[126]
142: R = *t*-Bu, Rh, 18(*S*)[126]



143: R = C_8F_{17}, Rh 5(*S*)[126]
144: R = $C_6H_3(C_8F_{17})_2$-3,.5, Rh, 10(*S*)[126]

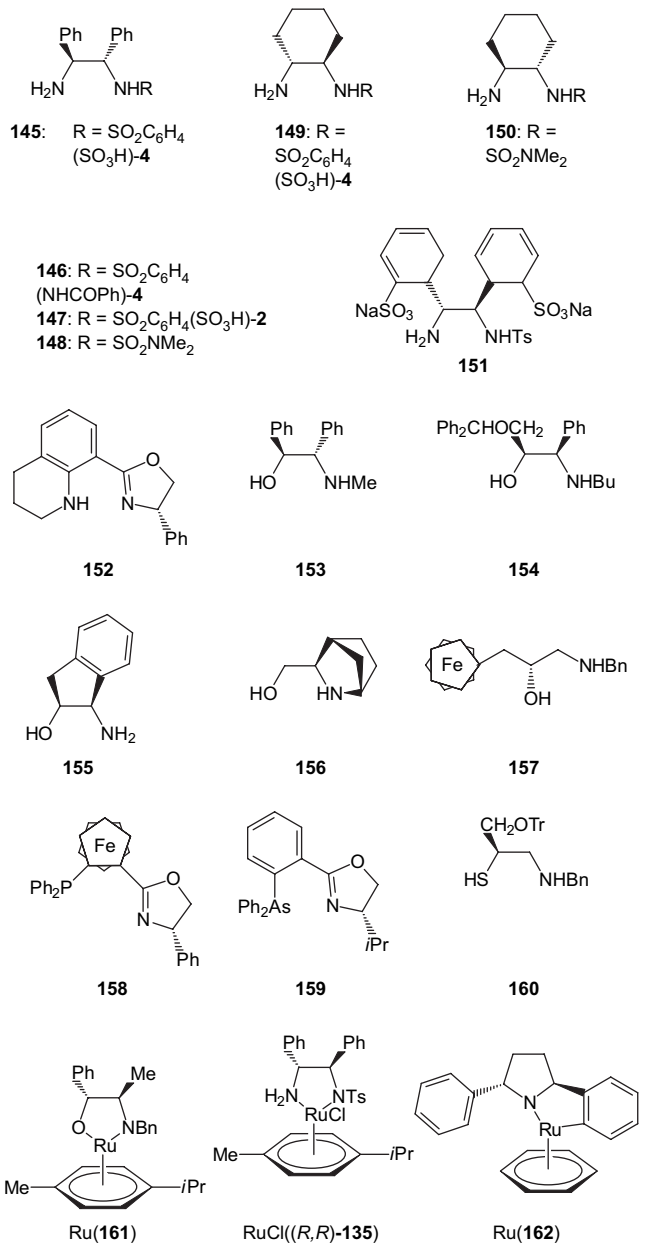
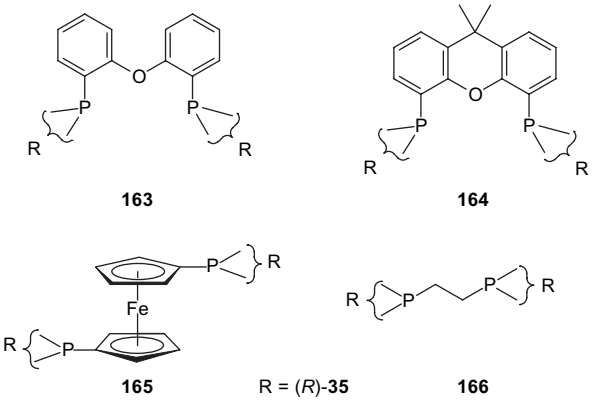


Table 5
Hydrogen transfer hydrogenation of acetophenone on Ru complexes with C_2- and C_1-symmetric bidentate ligands

Entry	Ligand (complexes)	Symmetry	ee [%] (config. of 1-phenylethanol)	Ref.
1	(*S*,*S*)-**122**	C_2	24(*R*)	115
2[a]	(*S*,*S*)-**135**	C_1	98(*S*)	127a
			97(*S*)	128
3	(*R*,*R*)-**135**	C_1	99(*R*)	127a
			90(*R*)	120
4	**145**	C_1	94(*S*)	129
5	**146**	C_1	96(*S*)	130
6	**147**	C_1	91(*S*)	129
7	**148**	C_1	96(*S*)	131
8	(*R*,*R*)-**136**	C_1	97(*R*)	121
9[b]	**149**	C_1	88(*R*)	129
10	**150**	C_1	94(*S*)	131
11	**151**	C_1	95(*R*)	132
12	**152**	C_1	83(*S*)	133
13	**153**	C_1	92(*S*)	134
14	**154**	C_1	72(*S*)	135
15	**155**	C_1	91(*S*)	136
16	**156**	C_1	94(*S*)	137
17	**157**	C_1	72(*R*)	138
18	**27**	C_1	94(*R*)	139
19	**158**	C_1	94(*S*)	140
20	**159**	C_1	82(*R*)	141a
21	**160**	C_1	83(*R*)	141b
22	Ru(**161**)	C_1	95(*R*)	142a,b
23[c]	RuCl((*R*,*R*)-**135**)	C_1	>99(*R*)	143
23	Ru(**162**)	C_1	89(*R*)	146

[a] Reaction 9 on Ru complexes with analogous C_1-symmetric chiral ligands (ee=97–99%), see Ref. 127b.
[b] Similar C_1-symmetric chiral ligands of Ru complexes as catalysts of this reaction (ee=89–96%), see Ref. 129.
[c] Reaction 9 on Ru complexes with analogous (ee=96%) or similar (ee=94–99%) C_1-ligands, see Ref. 144,145.

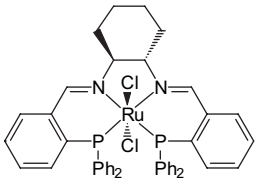


As can be seen, a high degree of enantioselectivity is specific for reaction 9 over ruthenium complexes only with asymmetric ligands. It is interesting to note that the Ru(**162**) complex will be asymmetric only after a reaction of $[Ru(\eta_6\text{-benzene})Cl_2]_2$ with C_2-symmetric chiral amine **162**.

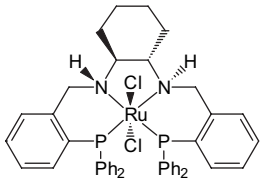
To the contrary, C_2-ligand **122** leads to a relatively smaller enantioselectivity. C_2-Ligands of the type **163**–**166** are probably not exceptional.[147]

Hydrogenation of acetophenone in similar reaction conditions and L*/Ru=1:1 results in the ee values: 17(*R*), 54(*R*), 0, 5(*R*), respectively. Maximal enantioselectivity of **164** (ee=93–97(*R*)) is achieved at L*/Ru=2.5–6. It is conceivable that the catalytic system attains the Ru/1.5L* or Ru/*n*L* structure, which has probably lost C_2 symmetry.

Thus, the experimental data point to the fact that rhodium, iridium and ruthenium complexes with chiral C_2- and C_1-symmetric bidentate ligands are differentiated by an enantioselectivity degree in reaction 9. Complexes with asymmetric ligands achieve this reaction with higher ee values of the product. The high enantioselectivity of reaction 9 over ruthenium complexes with tetradentate C_2-symmetric ligand **168** seems to be in conflict with this conclusion.[148,149]

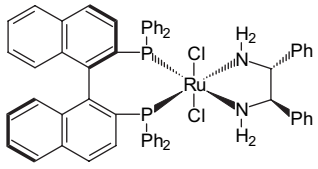


$RuCl_2$(**167**), 18(*R*)[148,149]



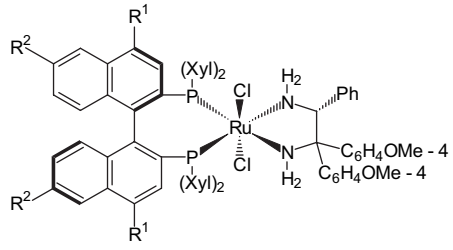
$RuCl_2$(**168**), 97(*R*)[148]

X-ray data[148] show that the molecular structure of $RuCl_2$(**167**) has approximate C_2 symmetry, whereas $RuCl_2$(**168**) has a more distorted C_2 geometry, due to the 'propeller' position of the *P*,*N*-phenyl rings. However, the C_2 symmetry distortion is probably not the main reason for the relatively higher enantioselectivity of $RuCl_2$(**168**). The $RuCl_2$((*R*)-**13**)((*R*,*R*)-**65**) complex as the catalyst of reaction 9 has a similarity with $RuCl_2$(**168**) (in dentate groups of ligands):[150,151]

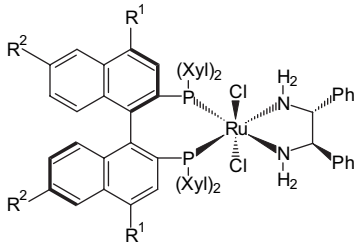


$RuCl_2$((*R*)-**13**)((*R*,*R*)-**65**), 83(*S*)[150,151]

Different versions of this system[151–158] have also been investigated in this reaction. The asymmetric induction step involves a simultaneous transfer of apical hydride at the Ru atom of *trans*-RuH(Cl)(diphosphine) (diamine) and a proton of the RNH_2 ligand to the carbonyl group via a six-membered transition state.[159] This step includes a monohydride intermediate that has lost its C_2 symmetry axis of the starting complex. An analogous mechanism exists probably in the event of Rh(**168**) as a catalyst of reaction 9 (Rh(**167**), ee=40(*S*),[149]



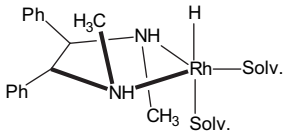
R^1 = TMS, R^2 = H, $RuCl_2$ ((*R*)-**169**)((*R*,*R*)-**170**), 99.8(*S*),[152b]
R^1 = R^2 = Me, $RuCl_2$ ((*R*)-**171**)((*R*,*R*)-**170**), 99.6(*S*),[152b]
R^1 = Ph, R^2 = Cl, $RuCl_2$ ((*R*)-**172**)((*R*,*R*)-**170**), 89.9(*S*)[152b]



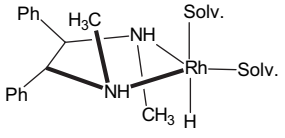
R^1 = TMS, R^2 = H, $RuCl_2$ ((*R*)-**169**)((*R*,*R*)-**65**),98.4(*S*)[152b]
R^1 = R^2 = Me, $RuCl_2$ ((*R*)-**171**)((*R*,*R*)-**65**), 98.5(*S*)[152b]
R^1 = Ph, R^2 = Cl, $RuCl_2$ ((*R*)-**172**)((*R*,*R*)-**65**), 87.9(*S*)[152b]

Rh(**168**), ee=89(*S*)[149]). It is of interest that systems of this type show a small negative leap in the product ee values at the transition from the complex with C_2-ligands **169**–**172** and C_1-ligand **170** to the corresponding C_2-symmetric complex with C_2-ligand ligand **65** in reaction 9:[152b]

The Rh(**120**)-type complexes have a stable metallacycle structure with the stereogenic nitrogen atom, according to DFT calculations.[110] For example, structures A and B are possible in the case of Rh((*R*,*R*)-**120**):



A

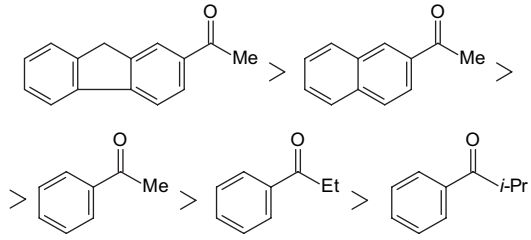


B

Formation of the above-mentioned six-membered transition state is possible over the NH–RhH bond (*proS* (or *proR*) of $R^1R^2C{=}O$ position) of A and equally under this bond (*proS* (or *proR*)) in complex B. In the case of the Rh(**65**, **126** or **128**)-type complexes, an additional two *proR* (or *proS*) of the carbonyl position are possible. Therefore, the enantioselectivity of the reaction on the Rh(**120**) complex will be higher than over Rh(**65**, **126** or **128**)-type complexes in accordance with the experimental data (Table 4). The enantioselectivity of the reactions on complexes with C_2-symmetric ligands of the **120**–**131** type should not be high, because of a possibility of the cis-position of bulky substituents. This is in accordance with the experimental data (Table 4).

The above-mentioned mechanism takes place, if asymmetric induction proceeds during the substrate coordination with the catalyst.

Indeed, we have found experimental evidence,[6a,118] that asymmetric induction in reaction 9 occurs during the substrate coordination by a hydride complex. There is an enantioselectivity decrease in reaction 9 on rhodium and iridium complexes of the Rh(**131**) type in a series of ketones as substrates:



In this series the difference between molecular volumes of the substituents of the carbonyl group of these ketones is reduced. The enantioselectivity drop in this series can be explained as a consequence of decreasing enantiodiscrimination with reduction of these molecular volume difference.

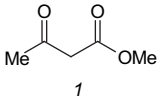
A direct proportion of these parameters can be considered as an argument in favour of the fact that asymmetric induction (chiral recognition) takes place in a direct interaction between a catalytic complex and substrate.

Thus, the enantioselectivity degree of hydrogen transfer hydrogenation of simple aryl alkyl ketones is dependent on the

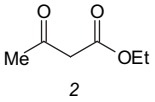
symmetry of these complexes. Complexes with chiral C_1-symmetric bidentate ligands catalyze this reaction with higher enantioselectivity than chiral C_2-symmetric complexes. In the case of complexes with C_2-symmetric tetradentate ligands of the $RuCl_2$(**168**) or $RuCl_2$(**13**)(**65**) type, the C_2 symmetry is lost prior to the asymmetric induction step.

5. Hydrogenation of ketopantoyllactone on Rh and Ru complexes

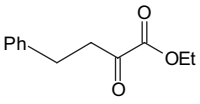
A very high enantioselectivity of hydrogenation of β-functionalized ketones on Ru complexes with C_2-symmetric ligands is well known.[160–162] It is believed[6] that coordination of these substrates by two vacancies of the metal atom is favourable for decreasing symmetry of the intermediate with the C_2-ligand,



1



2



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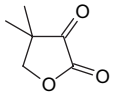
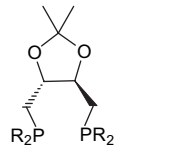
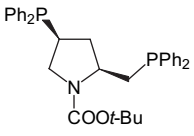


4

which is responsible for asymmetric induction. It has been supposed that the reaction of this type belongs to the category of reactions, which may give high enantioselectivity in the presence of C_2 auxiliaries. A comparison between the ee values of hydrogenation of β- and α-ketoesters *1–4* on [RuCl(*p*-cymene) ((*R*)-**13**)]Cl (or the $[RuCl_2(C_6H_6)]_2$-(*R*)-**13** catalytic system) shows that the enantioselectivity is far less in the case of cyclic α-ketoester *4* (ee=92(*R*), 93(*R*), 83(*R*), 56(*R*), respectively).[162] The cyclic structure of ketopantoyllactone *4* probably prevents a bidentate two-point coordination of these substrates. The enantioselectivity reduction in the hydrogenation of *4* can be explained by the behaviour of this substrate as a simple unfunctionalized ketone. Analogous to reactions 5 (without Ti(O-*i*-Pr)$_4$) and 9, an increase of enantioselectivity takes place when passing from C_2-**2**, **3**, **173**, **174** to C_1-**1**, **175–180** ligands in the hydrogenation of *4* on [Rh(COD)Cl]$_2$/L* complexes (Table 6).



173: R = *i*-Pr
174: R = $C_6H_4NMe_2$-*p*



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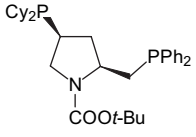

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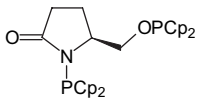

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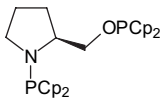

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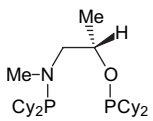

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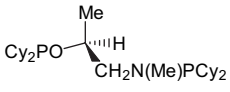


180

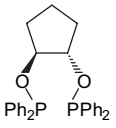
Table 6
Hydrogenation of ketopantoyllactone on [Rh(COD)Cl]$_2$/L* complexes with C_2- and C_1-ligands

Ligand	Symmetry	ee [%] (config. of product)	Ref.
2	C_2	52(*R*)	163
3	C_2	45(*R*)	163
173	C_2	54(*R*)	164
174	C_2	46(*R*)	165
1	C_1	75(*R*)	163
175	C_1	81(*R*)	166
176	C_1	92(*R*)	167
177	C_1	96(*R*)	168
178	C_1	76(*R*)	169
179	C_1	89(*S*)	170
180	C_1	80(*S*)	170

It can see from this table that there is a quantitative leap in enantioselectivity of the reaction on these complexes on changing from C_2- to C_1-ligands.

6. Hydrogenation of acetophenone and unfunctionalized arylalkenes on Rh, Ir, Ti, Zr and Sm complexes

Unfunctionalized olefins and ketones have not been studied in hydrogenation on rhodium complexes with modern ligands **4–20** that show very high enantioselectivity in hydrogenation of functionalized alkenes. There are few hydrogenation reactions of these substrates (***1–3***) on Rh complexes with C_2-bis(diphenyl)phosphine ligands that are characterized by relatively low ee values of the products (Table 7).



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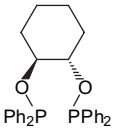

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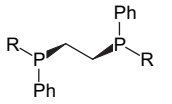
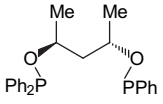


183: R = C_6H_4OMe-2



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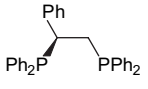

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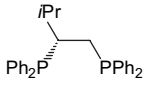

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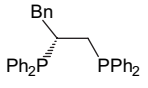

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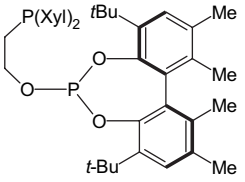


188

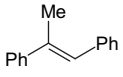
As seen from the table, a positive leap in enantioselectivity takes place at the transition from C_2-(**2**, **183**, **184**) to C_1-(**185–188**) ligands of Rh and Ir complexes in hydrogenation of

Table 7
Hydrogenation of ketones, unfunctionalized olefins and imines on rhodium and iridium complexes with chiral ligands

Ligand L	Symmetry	Complex	Substrate	ee [%]	Ref.
181	C_2	[RhCl(1,5-hexadiene)]$_2$/L	***1***	22(*R*)	171
(*S*,*S*-**2**)	C_2	[Rh(NBD)(L)]ClO_4	***1***	3(*S*)	172
(*S*,*S*-**2**)	C_2	[Rh(NBD)(L)]ClO_4	***1***	8(*R*)	173
(*S*,*S*-**2**)	C_2	[RhCl(hexadiene)]$_2$/L	***1***	38(*R*)	174
(*R*,*R*)-**2**	C_2	[RhCl(hexadiene)]$_2$/L	***2***	24(*S*)	171
182	C_2	[RhCl(hexadiene)]$_2$/L	***2***	33(*R*)	175
183	C_2	[RhCl(NBD)]$_2$/L	***5***	4(*R*)	176
(*S*,*S*-**2**)	C_2	[RhCl(NBD)]$_2$/L	***5***	3(*S*)	176
184	C_2	[RhCl(NBD)]$_2$/L	***5***	5(*S*)	176
185	C_1	[RhCl(NBD)]$_2$/L	***5***	64(*R*)	176
186	C_1	[RhCl(NBD)]$_2$/L	***5***	66(*S*)	176
187	C_1	[RhCl(NBD)]$_2$/L	***5***	72(*S*)	176
188	C_1	[IrCl(COD)]$_2$/L	***4***	84(*S*)	177

1

2



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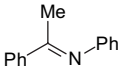

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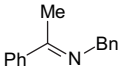

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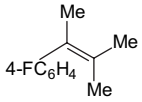
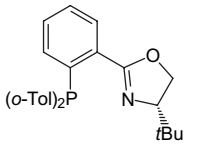


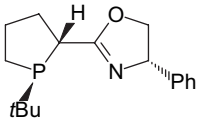
6

imines ***4*** and ***5***. A high enantioselectivity hydrogenation of unfunctionalized olefin ***3*** occurs in the presence of the iridium complex with C_1-symmetric *P*,*N*-ligands:[178–191]

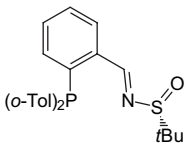
The ee values of the product of *E*-1,2-diphenylpropene hydrogenation on [Ir(L*)(COD)]$^+$ complexes are given below the corresponding ligands. A majority of these values fall within the range of 95–99% ee. Since C_2-bis(diphenyl)phosphine bidentate ligands **2**, **181** and **182** strongly differ in structure and electronic effects from C_1-*P*,*N*- and *N*,*N*-ligands **189**–**205**, the increase of the ee values of hydrogenation of *3* versus *2* (Table 7) is a necessary, but not sufficient, argument in favour of the assumption that hydrogenation of unfunctionalized olefins is highly enantioselective in the presence of C_1-symmetric chiral auxiliaries, and much higher than that on C_2-symmetric chiral additives.



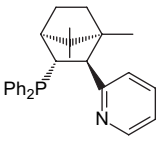
189, 97(*R*),[178,179] 98(*R*)[180]



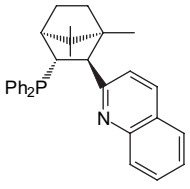
190, 95(*R*)[181]



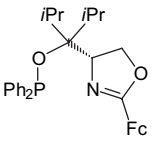
191, 94(*S*)[182]



192, 95(*S*)[183]

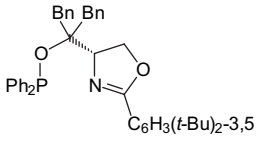


193, 95(*S*)[183,184]

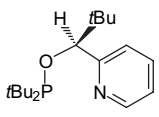


Fc — ferrocenyl

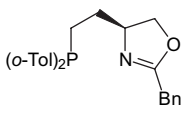
194, 97(*R*)[185a]



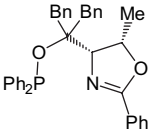
195, 98(*R*)[185a]



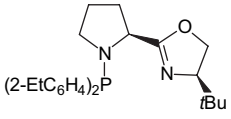
196, 97(*S*)[185b]



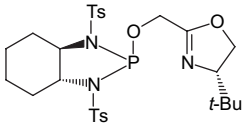
197, 95(*S*)[186]



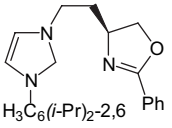
198, 99(*R*)[180]



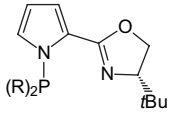
199, 92(*R*)[187]



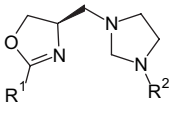
200, 94(*R*)[188]



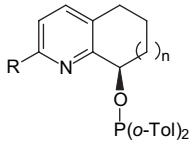
201, 98(*S*)[189]



202: R = *o*-Tol, 99(*R*)[179b]
203: R = Cyclohexyl, 99(*R*)[179b]

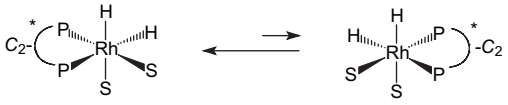


204: R^1 = Adamantyl, R^2 = $C_6H_3(i\text{-Pr})_2$ -2,6, 98(*S*)[190]



205: R = C_6H_4Me-*p*, 99(*R*)[191]

Hydrogenation of unfunctionalized C=C, C=O and C=N substrates proceeds with lower enantioselectivity on C_2-bis(diphenyl)phosphine rhodium complexes in comparison with functionalized substrates over the same catalysts.[6c] It is assumed that all these regular trends originate from the structure of the intermediate complexes that controls the asymmetric induction step. The equilibrium A ⇄ B has been identified spectroscopically in the case of reaction 1 on complexes of the Rh(**5**) type.[192]



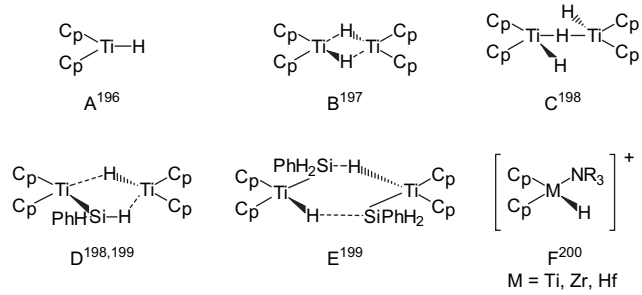
The arrangement of the atoms closely surrounding the metal atom in structures A and B is enantiomerical. A reaction through these dihydride intermediates may result in different product configurations. Functionalized substrates, which are coordinated by two points in a bidentate manner in the intermediates, are likely to have more limited degrees of freedom in choosing between A and B as compared to unfunctionalized substrates. This situation takes place in reaction 1 and in the hydrogenation of β-functionalized ketones.[160–162] Consequently, the reaction enantioselectivity in this case should be higher, as prompted by the experimental observation.

In hydrogenation on complexes with C_1-symmetric ligands, the equilibrium between A and B may shift to A to a greater extent than in the case of complexes with C_2-ligands. This brings about an enantioselectivity rise if unidentate coordinated unfunctionalized olefins, imines and ketones are involved in hydrogenation, in line with the experimental data.

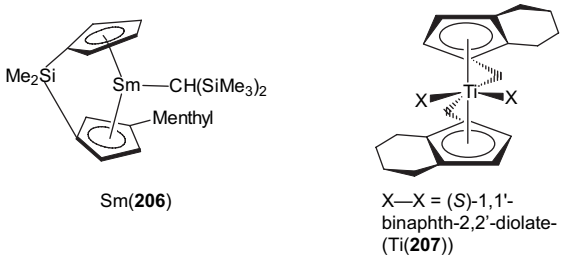
Asymmetric hydrogenation of acyclic aromatic *N*-arylimines on the Ir complex with the C_1-ligand (ee ≅ 90%)[193] reinforces this viewpoint.

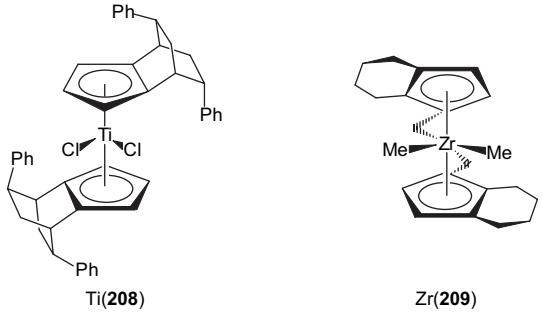
Titanocene and zirconocene are widely used as hydrogenation catalysts upon activation with $PhSiH_3$, *n*-BuLi, etc.[194] The following complexes with the ligands **206–210** have been applied as precursors of chiral catalysts:

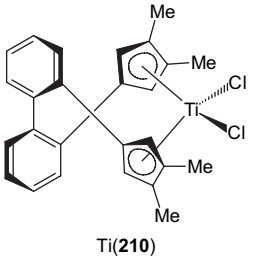
The intermediate complexes of olefin hydrogenation and hydrosilylation[195] on titanocene and zirconocene have been identified as hydrides and hydride dimers A–F (Scheme 4).[196–200]



Scheme 4.







Experimental data on the hydrogenation of unfunctionalized olefins and imines on Ti, Zr and Sm Cp-complexes are summarized in Table 8. As evident from the table, high enantioselectivity is observed where the reactions run only through the C_1-symmetric intermediate. The low enantioselectivity of the reaction on complexes of the C_2-(η^5-((−)menthyl)Cp)$_2$TiCl$_2$ and C_1-(η^5-((−)menthyl)Cp)((η^5-Cp)TiCl$_2$ type (ee = ∼10%)[208] can be explained by a missing Cp–Cp bridge in the complex structure. This bridge fixes a rigid arrangement of chiral substituents with respect to the metal atom (reaction centre) as, for example, in the Sm(**206**) complex. An analogous function in the highly enantioselective reaction on the Ti(**208**) complex might be performed by a counter position of the Ph groups that prevents the Cp-group rotation.

Thus, the enantioselectivity increase in the hydrogenation of unfunctionalized olefins, imines and ketones is observed during the movement from C_2- to C_1-symmetric ligands of Rh and Ir complexes. For Ti, Zr and Sm Cp-complexes, as catalysts, a more enantioselective reaction takes place in the case of C_1-symmetric (asymmetric) intermediate complexes controlling the asymmetric induction step. Hydrogenation of unfunctionalized olefins and imines on titanocene-type complexes belongs to the reactions which are independent of C_2–C_1 symmetry of chiral catalyst precursors. In these reactions, a C_2 symmetry loss occurs at the stage prior to the asymmetric induction step. If the intermediate which controls asymmetric induction retains C_2 symmetry of C_2 chiral auxiliaries, the enantioselectivity will be low.

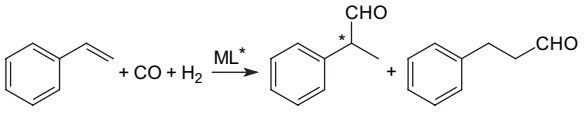
Therefore, hydrogenation of unfunctionalized substrates proceeds by different mechanisms, depending on the Rh or Cp–Ti groups of the catalysts.

Table 8
Hydrogenation of unfunctionalized olefins and imines on Ti, Zr, Sm complexes with chiral C_1- and C_2-symmetric ligands

Catalytic system	Intermediate controlling the asymmetric induction step				ee [%] (config. of product)	Ref.
	Possible structure	Symmetry	Ref.	Substrate		
[Ti(**207**)]+284[(Al(Me)–O)$_n$]	A	C_2	196	***2***	36(*S*)	201
Sm(**206**)	1/2 B or 1/2 C	C_1	197–199	***2***	96(*S*)	202
[Ti(**207**)]+2[*n*-BuLi]+2.5[PhSiH$_3$]	1/2 B, 1/2 C, 1/2 D or 1/2 E	C_1	197–199	***3***	>99(*R*)	203
[Ti(**208**)]+[*n*-BuLi]	1/2 B or 1/2 C	C_1	197, 198	***2***	68–95(*S*)	204
[Zr(**209**)]+[PhMe$_2$NH]$^+$[B(C$_6$F$_5$)$_4$]$^-$	F	C_1	200	***6***	96(*S*)	205
[Ti(**207**)]+2[*n*-BuLi]+2.5[PhSiH$_3$]	1/2 B, 1/2 C, 1/2 D or 1/2 E	C_1	197–199	***5***	77–85(*R*)	206
[Ti(**210**)]+2[*n*-BuLi]	1/2 B or 1/2 C	C_1	197, 199	***5***	76(*S*)	207

7. Hydroformylation of styrene over Rh and Ir complexes

Hydroformylation of olefins on chiral metal complexes is an example of a well-studied reaction[209] with a view to its commercial applications.[209b,210] Among the most extensively investigated reactions is styrene hydroformylation:

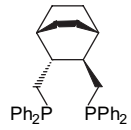


(10)

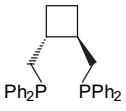
A list of chiral C_2-symmetric ligands **2**, **13**, **211**–**234** in rhodium and platinum complexes as catalysts of reaction 10 is given below, along with the product ee (configuration):[209a–c,209g,211–226]

Low ee values have attracted our attention in reaction 10 on rhodium complexes with chiral C_2-symmetric bis-(diphenyl)phosphine ligands **2**, **13**, **116** and **211**–**213**. The enantioselectivity of the platinum complexes is relatively higher. Bulky cyclic fragments at the phosphorus atoms in the ligands **214**–**224** contribute to the enantioselectivity increase. Nevertheless, the ee values of the reaction on the most complexes, for example, with C_2-ligands **225**–**234** are rather low. Strange as it may seem, the complex Rh/**232** catalyzes reaction 10 with zero enantioselectivity. Chiral C_2-symmetric ligand **232** includes conformationally rigid bicyclic systems at the phosphorus donor atoms. The rhodium complex with this ligand is probably the most rigorous C_2-symmetric complex mentioned above.

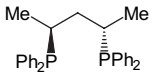
A quantitative enantioselectivity leap is observed at the transfer to the asymmetric complexes with C_1-ligands **235**–**247** acting as catalysts. The corresponding ligands and ee values of reaction 10 product are listed below:[209a,227–235]



211, Pt, 25(*S*)[209c]

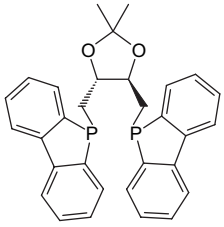


212, Rh, 4(*R*)[209g] 3(*R*)[211]

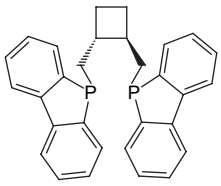


213, Rh, 5(*R*)–60(*S*)[212]; Pt, 10(*R*)–75(*S*)[213]

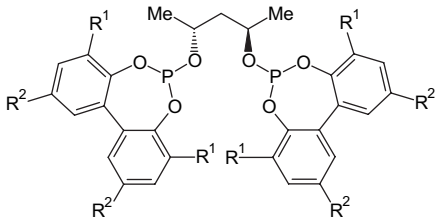
116, Rh, 24(*R*)[209g]
(*R*)-**13**, Rh, 25(*S*)[212];(*S*)-**13**, Pt, 19(*R*)–69(*S*)[214]
(*R*,*R*)-**2**, Pt, 12–36(*S*),[215] 4(*S*),[209g] 29(*S*);[209b]
Rh, 12(*R*),[211] 18(*R*),[216] 10(*R*)[209g];
(*S*,*S*)-**2**, Rh, 12(*S*)[212]



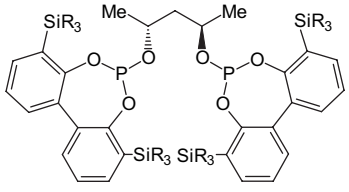
214, Pt, 64(*S*),[217] 80(*S*)[218]
Rh, 25(*S*),[211] 37(*S*)[216]



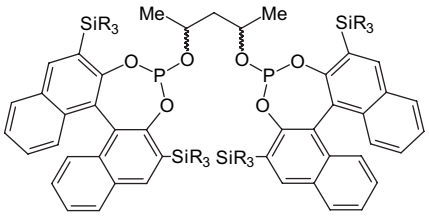
215, Rh, 40(*S*),[209g] 27(*S*)[211]



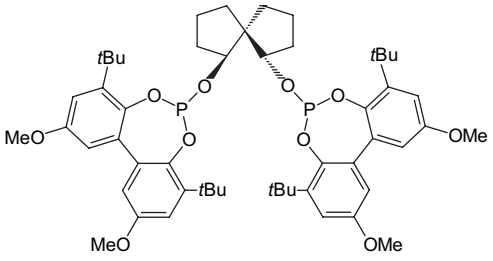
216: R^1 = R^2 = H, Rh, 14(*S*)[209g]
217: R^1 = R^2 = *t*-Bu, Rh, 68(*S*),[219] 44–90(*S*)[209g]
218: R^1 = *t*-Bu, R^2 = OMe, Rh, 61(*S*)[209g]



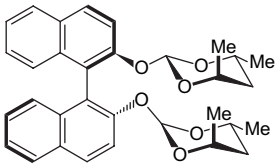
219:R = Me, Rh, 53–87(*S*)[220]
220:R = Et, Rh, 25–34(*S*)[220]
221:SiR$_3$ = SiMe$_2$*t*-Bu, Rh, 20(*S*)[220]



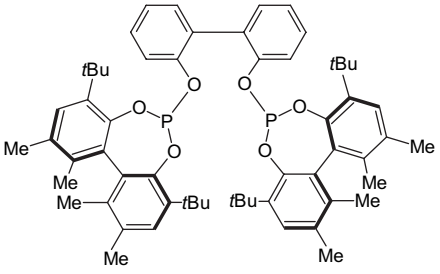
(2*R*,4*R*),(*R*/*S*)$_{ax}$-**222**: R = Me, Rh, 21–47(*S*)[220]
(2*R*,4*R*),(*R*)$_{ax}$-**222**: R = Me, Rh, 38(*S*)[209a]
(2*R*,4*R*),(*S*)$_{ax}$-**222**: R = Me, Rh, 69–86(*S*)[209a]
(2*S*,4*S*),(*R*)$_{ax}$-**222**: R = Me, Rh, 23(*S*)[209a]
(2*S*,4*S*),\(*S*)$_{ax}$-**222**: R = Me, Rh, 40(*R*)[209a]
(2*R*,4*R*),(*R*/*S*)$_{ax}$-**223**: R = Et, Rh, 20–28(*S*)[220]



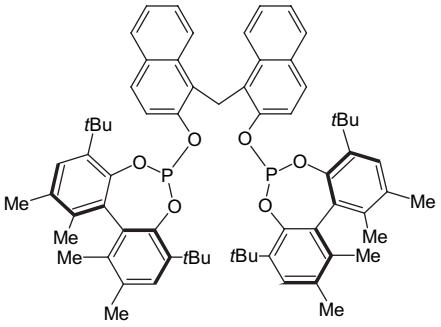
224, Rh, 69(*S*)[221]



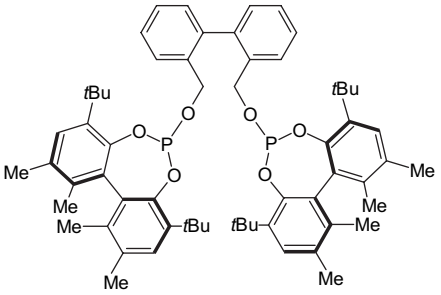
(R_{ax})-**225**, Pt, 23(R)[222]
(S_{ax})-**225**, Rh, 20(S)[222]



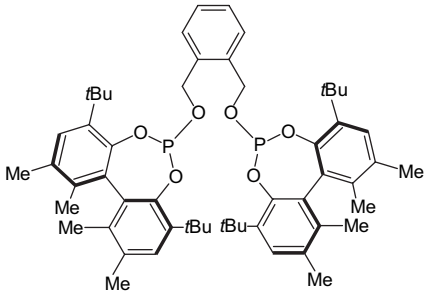
226, Rh, 18(*R*)[223]



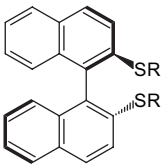
227, Rh, 9(*S*)[223]



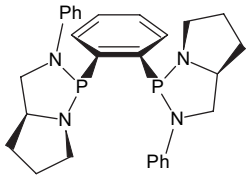
228, Rh, 37(*S*)[223]



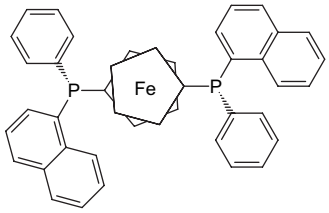
229, Rh, 19(*R*)[223]



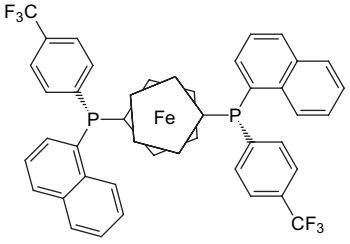
230: R = H, Rh, 7–11(*S*)[224]
231: R = Me, Rh, 2–5(*S*)[224]



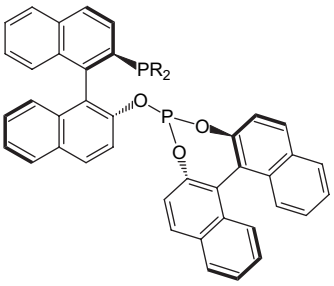
232, Rh, *ee* = 0%[225]



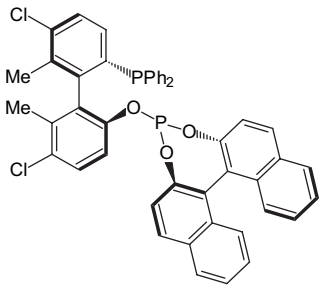
233, Rh, 46(*S*)[226]



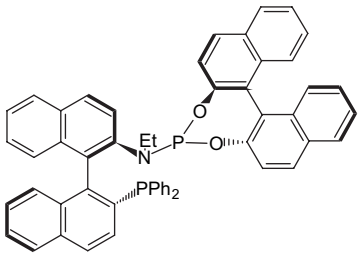
234, Rh, 50(*S*)[226]



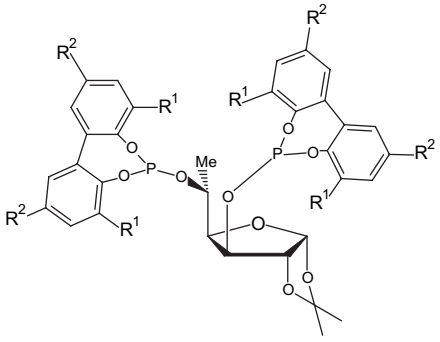
(*R*,*S*)-**235**: R = Ph, Rh, 95(*R*)[227] 94(*R*)[228]
(*S*,*R*)-**235**: R = Ph, Rh, 94(*S*)[229]
236: R = 3-MeO-C_6H_4, Rh, 97.5(*R*)[230]
237: R = 3-*i*-PrO-C_6H_4, Rh, 98.3(*R*)[230]
238: R = 3-Me-C_6H_4, Rh, 94.1(*R*)[230]
239: R = 3-$C_6F_{13}(CH_2)_2$-C_6H_4, Rh, 90.6(*R*)[228]
240: R = 3,5-$(MeO)_2$-C_6H_3, Rh, 92.2(*R*)[230]
241: R = 4-MeO-C_6H_4, Rh, 91.7(*R*)[230]



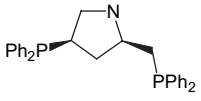
242: Rh, 94(*S*)[231]



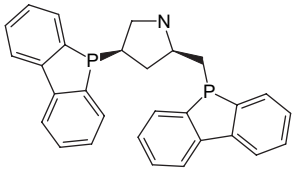
243: Rh, 99(*R*)[232]



244: R^1 = *t*-Bu, R^2 = OMe, Rh, 90(*S*)[233]
245: R^1 = $SiMe_3$, R^2 = H, Rh, 93(*S*)[209a]



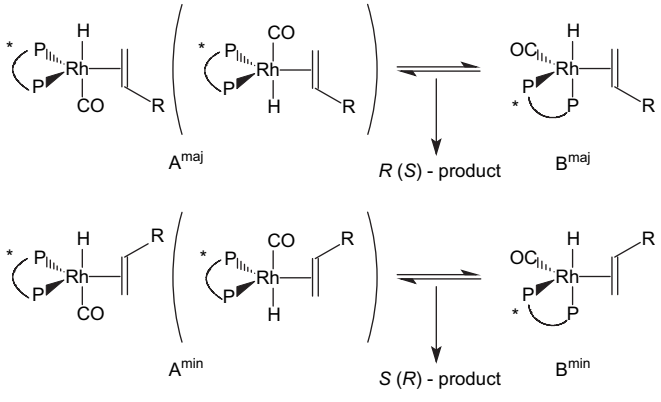
246, Pt, >96(*S*)[234]



247, Pt, >96 (configuration is not indicated)[235]

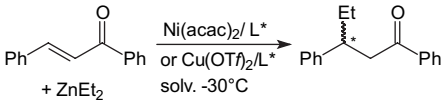
A mechanism for reaction 10 on rhodium complexes with diphosphine ligands[210a,227] proposed recently is based on an equilibrium of two pairs of diastereomeric intermediates[236] in the trigonal bipyramidal form:

These intermediates are introduced into 'major' and 'minor' catalytic cycles and are responsible for the asymmetric induction. If reaction 10 proceeds in the presence of chiral C_2-symmetric complexes and the equilibrium between intermediates A and B is established rather rapidly, $A^{maj}=A^{min}$ and $[A^{maj}]\approx[A^{min}]$, the product would have a low ee value. Chiral C_1-symmetric (asymmetric) complexes catalyze the reaction with higher enantioselectivity than chiral C_2-symmetric complexes, because of $A^{maj}\neq A^{min}$ and $[A^{maj}]\neq[A^{min}]$. Thus, a dependence of the product ee values on the symmetry of the complexes acting as catalysts is observed in the hydroformylation of olefins on diphosphine complexes of rhodium.



8. Conjugate addition of diethylzinc to chalcones on Cu and Ni complexes

Conjugate addition of dialkylzinc to α,β-unsaturated prochiral enones is an efficient and reliable method for the synthesis of optically active β-substituted carbonyl compounds.[237] Chalcones are suitable substrates for this reaction.



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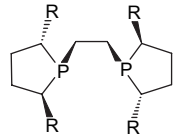
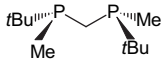
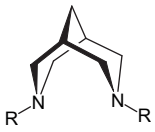


Cu(OTf)$_2$/**248**: R = Me, 0%[238]

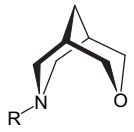


Cu(OTf)$_2$/**249, 71** (*R*)[239] (–80°C)

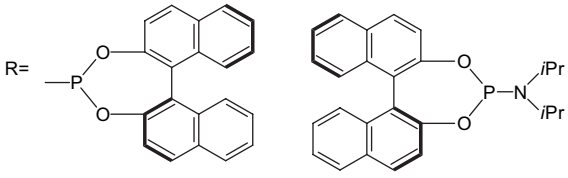
Cu(OTf)$_2$/**7**: R = Et, 7(*R*)[238]



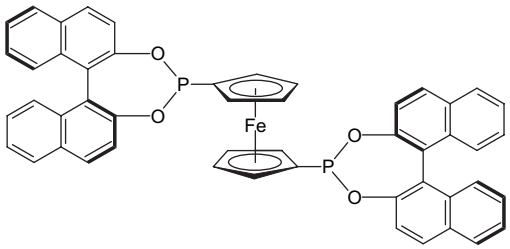
Cu(OTf)$_2$/**250**, 78(*S*)[237b]



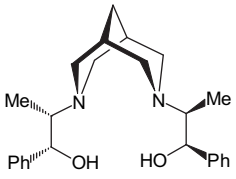
Cu(OTf)$_2$/**251**, 82(*S*)[237b,240]



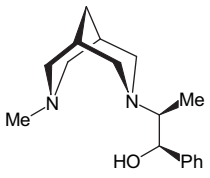
Cu(OTf)$_2$/**252**, 83[241]



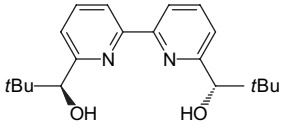
Cu(OTf)$_2$/**253**, 69–71(*S*)[242]



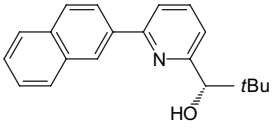
Ni(acac)$_2$/**67**, 0%[85]



Ni(acac)$_2$/**66**, 79(*S*)[85]



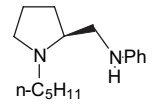
Ni(acac)$_2$/**254**, 72(*R*)[243]



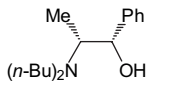
Ni(acac)$_2$/**255**, 86(*R*)[244]

The use of C_2-symmetric ligands in reaction 11 leads to contradictory results.[85,237b,238–244]

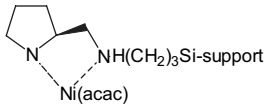
On the one hand, complexes with C_2-bidentate ligands **7**, **248** and tetradentate ligand **67** afford a very small enantioselectivity in reaction 11 and, on the other hand, complexes



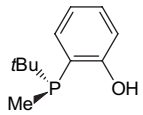
NiCl$_2$/**256** 82(*S*)[245]



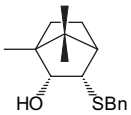
Ni(acac)/**257**/2,2'-Bipyridyl, 90 (*R*)[246]



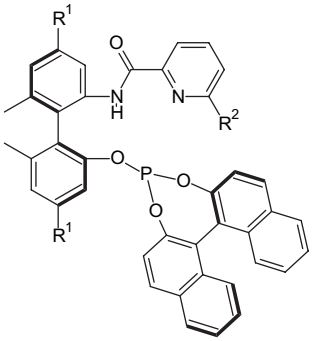
258, 91[247]



CuOTf/**259**, 82(*S*)[248]

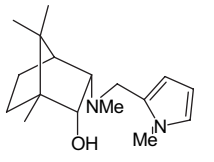


Ni(acac)$_2$/**260**, 86(*S*)[249]

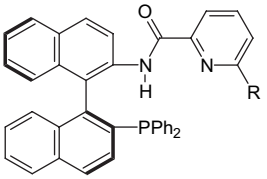


[Cu(MeCN)$_4$]BF$_4$/L*

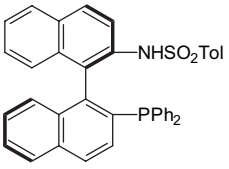
R^1	R^2	L*	*ee*
H	H	**261**	94(*S*)[250]
Me	Me	**262**	97(*S*)[250]



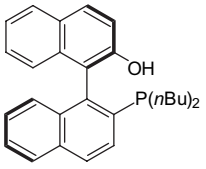
Ni(acac)$_2$/**263**, 83(*S*)[251]



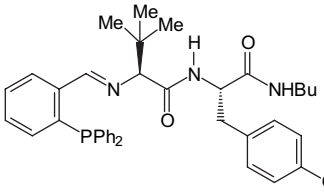
Cu(Otf)$_2$/**264**, 96(*S*)[252]



Cu(OTf)$_2$/**265**, 94(*R*)[253a] (benzylideneacetone)



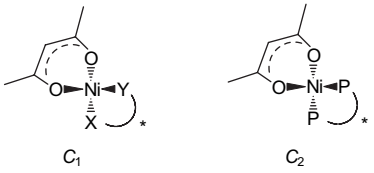
Cu(OTf)$_2$/**266**, >99(*R*)[253b] (–50→ 0°C)



Cu(OTf)$_2$/**267**, 93(*S*)[254] (benzylideneacetone)

with C_2-**249**, **253** lead to moderate ee value of the product in this reaction. The product ee values and configurations in the reaction on complexes with C_2-bidentate **250** or C_2-tetradentate **254** ligands actually coincide with the enantioselectivity data for this reaction over complexes with corresponding C_1 fragments (**251**, **252** or **255**). This implies that bidentate and tetradentate C_2-symmetric ligands are most probably involved in the reaction by their C_1-symmetric fragments. Thus, the complexes with C_2-ligands catalyze this reaction with enantioselectivities in the range from 0 to 70% ee.

In parallel with C_1-**255**, the best results have been achieved where C_1 chiral auxiliaries were used:[245–254] It can be assumed that the structure of the important intermediate complex[243b] of reaction 11 on Ni(acac)$_2$ complexes and C_1-ligands of the type **255**–**267** should be C_1-symmetric.

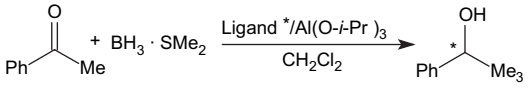


There are grounds for assuming that this intermediate is involved in the reaction at the asymmetric induction stage. In the case of C_2-symmetric ligands of the type **7**, the structure of the intermediate is C_2-symmetric. As concerns the above-mentioned reactions, if the intermediate responsible for asymmetric induction retains the symmetry of the starting ligands, this reaction gives better results with C_1 auxiliaries. This assumption reflects exactly the experimental data for reaction 11.

α-Ketoolefin chalcones as well as α-ketoether ketopantoyllactones drop out of the unfunctionalized aldehydes, ketones and olefins as substrates of the above-mentioned reactions. It seems likely that α-functionalized olefins and ketones of the chalcone and ketopantoyllactone types along with unfunctionalized substrates are coordinated only by a single vacancy of the metal atom in the intermediate complex.

9. Other catalytic and stoichiometric reactions with the participation of metal complexes

In reaction 12 of acetophenone reduction by borane addition of Al(O-*i*-Pr)$_3$ to the reaction mixture containing chiral C_2-symmetric atropoisomeric ligands[255] (Table 9) leads to an enantioselectivity rise. This behaviour is reminiscent of the diethylzinc addition to benzaldehyde on chiral C_2-symmetric ligands, both without Ti(O-*i*-Pr)$_4$ and in its presence (Table 3).

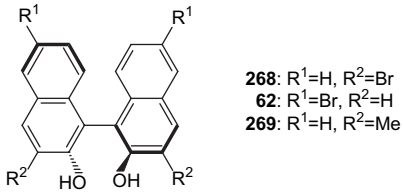


(12)

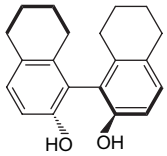
Therefore, this phenomenon could be explained in a similar way. In all likelihood, the reaction mixture incorporating borane, the C_2-symmetric ligand and Al(O-*i*-Pr)$_3$ forms an 'in situ' asymmetric complex, which is catalytically active and responsible for the asymmetric induction.

Table 9
Asymmetric acetophenone reduction by borane in the presence of chiral C_2-symmetric ligands and Al(O-*i*-Pr)$_3$ (CH_2Cl_2, rt)[255]

Entry	Ligands	Reaction systems			
		PhCOMe/BH_3·SMe_2/ligand		PhCOMe/BH_3·SMe_2/ligand/Al(O-*i*-Pr)$_3$	
		Yield [%]	ee [%] (config. of product)	Yield [%]	ee [%] (config. of product)
1	(*R*)-**35**	78	0	97	60(*S*)
2	**268**	90	0	94	46(*R*)
3	**62**	96	0	98	0
4	**269**	93	0	97	10(*R*)
5	**36**	91	0	95	71(*S*)

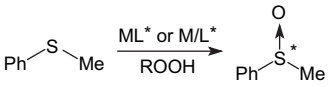


268: R^1=H, R^2=Br
62: R^1=Br, R^2=H
269: R^1=H, R^2=Me



36

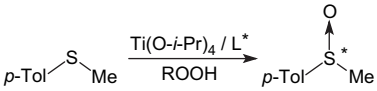
The symmetry of the chiral catalysts is of considerable importance in the enantioselective oxidation of thioanisole with hydroperoxides.



(13)

As evident from Table 10, the complexes with C_1-symmetric chiral ligands **274**–**276** are much more effective in reaction 13 than the C_2 auxiliaries **270**–**273** of similar structure.

An amazing example of the ee sensitivity of a catalytic reaction to chiral ligand symmetry can be seen in the sulfide oxidation reaction 14 of an analogous sulfide on Ti(O-*i*-Pr)$_4$/L* complexes:

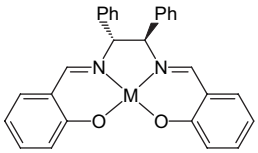


(14)

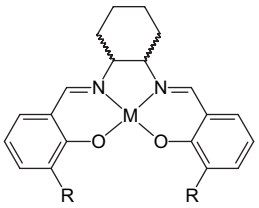
Table 11 sets out the reaction results with regard to the structure of chiral diols as ligands. Comparing the conformational rigidity of the complexes with these ligands, it should be possible to trace a rough row of possible divergences from ideal C_2 symmetry: Ti/**277**<Ti/**278**≪Ti/**279**≈Ti/**280**≈Ti/**61**. The complexes with the latter three ligands have maximal divergences from ideal C_2 symmetry in this row, due to possible rotation of COOEt, *t*-Bu and Ph groups at the asymmetric carbon atoms of the ligands around the C*–C bond. As seen from the table, this row coincides with the row of ee values of the product of reaction 14 on the complexes with these ligands. Hence, these reaction parameters are directly proportional: the greater divergences from ideal C_2 symmetry, the higher the enantioselectivity values.

Table 10
Asymmetric oxidation of thioanisole with hydroperoxides on chiral metal complexes

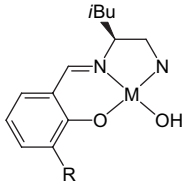
Ligand (L*)	Symmetry	Complex (ML* or M/L*)	Solvent, T (°C)	Hydroperoxide	ee [%] (config. of product)	Ref.
270	C_2	TiO(**270**)	CH_2Cl_2, 2	H_2O_2	3(*S*)	256
271	C_2	$(TiCl)_2O$((*R*,*R*)-**271**)	CH_2Cl_2, 0	*t*-BuOOH	8(*R*)	257
272	C_2	VO((*R*,*R*)-**272**)	CH_2Cl_2, 0	*t*-BuOOH	16(*S*)	258
273	C_2	MnCl((*S*,*S*)-**273**)	CH_3CN, rt	H_2O_2	14(*S*)	259
274	C_1	VO(**274**)	CH_2Cl_2, 0	30% H_2O_2	91(*S*)	260
275	C_1	$VO(acac)_2$/**275**	$CHCl_3$, rt	H_2O_2	96.7(*R*)	261
276	C_1	$VO(acac)_2$/**276**	CH_2Cl_2, 0	H_2O_2	86(*S*)	262



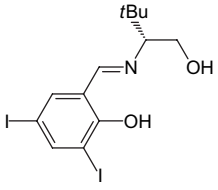
270
M=TiO



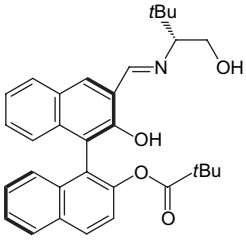
271:R=H; **272**: R=OMe; **273:** R=*t*Bu;
M=1/2$(TiCl)_2O$M=VO M=MnCl



274
M=VO

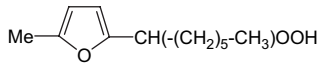


275

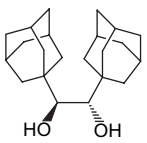


276

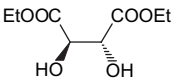
Table 11
Enantioselectivity-ligand structure dependence of aryl Me–S–*p*-tolyl oxidation

Entry	Ligand (L*)	Reaction mixture, solvent and temperature	Hydroperoxide	ee [%] (config. of product)	Ref.
1	**277**	Ti(O-*i*-Pr)$_4$/L*, MS 4 Å, Tol., −20 °C	*p*-$C_3H_7C_6H_4OOH$	0	263
2[a]	**278**	Ti(O-*i*-Pr)$_4$/L*, MS 4 Å, Tol., −20 °C	*p*-$C_3H_7C_6H_4OOH$	14[a]	263
3	**279**	Ti(O-*i*-Pr)$_4$/L*/*i*-PrOH, MS 4 Å, CH_2Cl_2, −20 °C	*p*-$C_3H_7C_6H_4OOH$	95.6(*R*)	264
4	**279**	Ti(O-*i*-Pr)$_4$/L*/H_2O, CH_2Cl_2, −20 °C	*t*-BuOOH	91(*R*)	265
5	**279**	Ti(O-*i*-Pr)$_4$/L*, $ClCH_2CH_2Cl$, −20 °C	*t*-BuOOH	88.3(*R*)	266
6	**279**	Ti(O-*i*-Pr)$_4$/L*, CH_2Cl_2, −20 °C		89(*R*)	267
7	**280**	Ti(O-*i*-Pr)$_4$/L*, MS 4 Å, Tol., −20 °C	*p*-$C_3H_7C_6H_4OOH$	95(*S*)	268
8	**61**	Ti(O-*i*-Pr)$_4$/L*, CCl_4, 0 °C	*t*-BuOOH	>99(*S*)	269

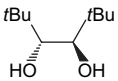
277



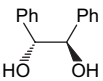
278



279



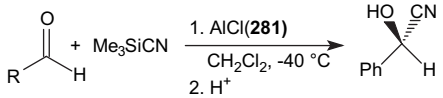
280



61

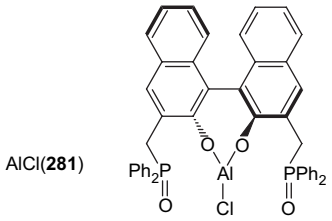
[a] Configuration not indicated.

Finally, an additional set of experimental data facilitate a possible explanation of the enantioselectivity increase due to the C_2 symmetry loss by the intermediate responsible for asymmetric induction of the reaction in the presence of chiral C_2-symmetric complexes. A large number of experimental observations indicate that the reaction enantioselectivity increases after the addition of achiral ligands or co-catalysts to the reaction mixtures (see review in Ref. 270). A typical example is the reaction of aldehyde cyanosilylation[271a] 15 in the presence of chiral Lewis acids as catalysts.



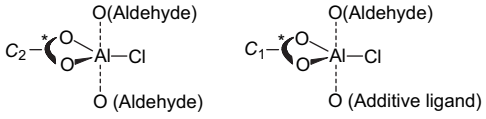
(15)

This reaction proceeds with a rather high enantioselectivity in the presence of the achiral ligand $Bu_3P(O)$:



R	Achiral ligand	*ee*% (conf.)
$PhCH_2CH_2$	$Bu_3P(O)$	97(*S*)
$PhCH_2CH_2$	–	9(*S*)
i-Pr	$Bu_3P(O)$	90(*S*)
i-Pr	–	25(*S*)

It has been shown that this reaction passes through an intermediate with a trigonal bipyramidal structure.[272,273]

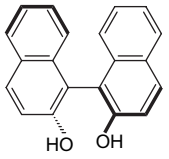


In contrast to the reaction without any additional achiral ligand, the intermediate in the presence of this additive loses the C_2 axis symmetry observed in the first intermediate. Hence, the enantioselectivity value increase may be explained by a decrease of intermediate symmetry from the C_2- to C_1-axis. From publications not included in the review,[270] worth mentioning are a similar effect of achiral ligand addition in the reduction of ketones by chiral diol-modified lithium aluminium hydride reagents[271b] and the Mannich reaction.[274] A somewhat less strong effect of achiral ligand addition can be seen in allylic alkylation,[275] epoxidation,[276,277] cyclopropanation,[278] cyanosilylation[279] and some other reactions on metal complexes.[280]

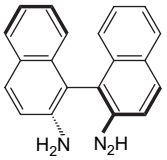
Numerous examples of using molecular sieves (MS 4 Å) are known to be a factor that increases the enantioselectivity of catalytic reactions in the presence of chiral C_2-symmetric metal complexes (see more recent publications, e.g., Refs. 281–284). This effect can also be explained by a loss of C_2 symmetry of the intermediate responsible for asymmetric induction in the reaction under the action of a chiral C_2-symmetric complex. Indeed, it is common for metal complexes of this type to be adsorbed by apical vacancies on the surface of chemosorbents. In this case, the C_2 symmetry axis of a catalytic complex is failing. As a result of adsorption, the intermediate complex on the adsorbent surface is asymmetric.

Mikami and Matsukawa[285] have proposed an alternative explanation for the enantioselectivity increase of the reactions under the action of catalytic complexes formed in situ with chiral C_2-symmetric ligands as a result of the addition of ancillary ligands. Sometimes, the effect of ancillary ligand addition is so high that the product configuration may change.[286]

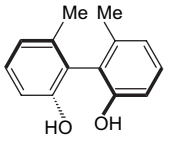
The abnormally low effectiveness of chiral C_2-symmetric auxiliaries is not limited only by catalytic reactions. For example, we[287,288] and other researchers[289–291] observed an abnormally low enantioselectivity of acetophenone reduction by chiral dihydrides produced from lithium aluminium hydride[§] and atropoisomeric ligands ($Li(H_n^*\overset{X}{\frown}\underset{X}{H_n})AlH_2$) listed below:[271,287,289–292]



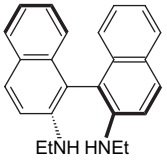
(*R*)-**35**, 2(*R*)[289], 0[287]



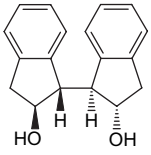
128, 9(*R*)[287]



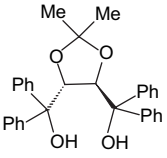
282, 2(*R*)[291]



283, 43(*S*)[290]



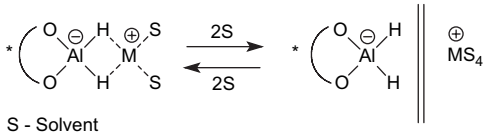
284, 14(*S*)[271]



285, 78(*S*)[292]

As the AlH_4^- anion in $LiAlH_4$ has an ideal tetrahedral structure, dihydride particles on the basis of ligands of the **35**, **128**, **282**–**285** type are chiral C_2-symmetric. The C_2 symmetry is also very close to perfect in this case. The Et group introduction to ligand **128** increases possible divergences from an ideal C_2 symmetry, as can be seen in dihydride Li(**283**)AlH_2, compared to dihydrides based on ligands **35**, **128**, **282** and **284**. This change in the C_2 symmetry quality is accompanied by the enantioselectivity increasing. The same explanation of ee increasing is also valid in the case of Li(**285**)AlH_2. The C_2 symmetry of this dihydride is not perfect because of four Ph groups, which can rotate around the $C-C_{Ph}$ bond. Consequently, the explanation of the influence of the chiral auxiliary symmetry on the enantioselectivity of catalytic reactions is also valid in the case of stoichiometric reactions.

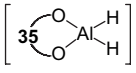
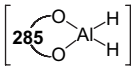
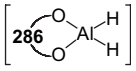
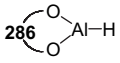
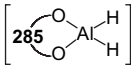
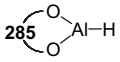
As with pure $LiAlH_4$ and $NaAlH_4$, dihydrides modified by diols react with ketones in THF or diglyme as contact and solvent-separated ion pairs.[293]



[§] Noyori and co-workers[289] supposed that the disproportionation of Li(BINOL)AlH_2 into $LiAlH_4$ and $LiAl(BINOL)_2$ is the reason for the low enantioselectivity of ketone reduction by this dihydride, yet this idea has not been supported by experiment. It has been shown by us[287] that this disproportionation does not proceed under the discussed reaction conditions.

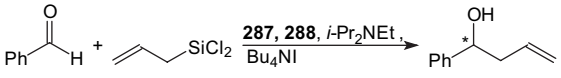
Given a lower strength of the hydride bond with Na^+ cations compared to that of Li^+ cations, it is believed that the bridge cycle is more rigid in the case of Li. Therefore, C_2 symmetry is closer to perfect in lithium than in sodium dihydride. In turn, a cycle formed by the ligand is more rigid in monohydride based on AlH_3 than on $NaAlH_4$. Thus, C_2 symmetry of the monohydride based on AlH_3 is much closer to perfect. In terms of these correlations, hydrides can be arranged in rows based on divergences from ideal C_2 symmetry (ligand **286** is an analogue of **285**, Ar=C_6H_4OMe-4) (Table 12).

Table 12
Enantioselective reduction by chiral aluminium hydrides[287,288]

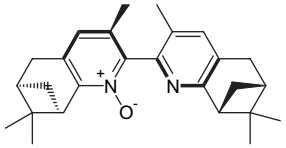
Substrate	Complex with aluminium hydride	Cation	ee [%] (config. of product)
PhCOMe		Na Li	38(*S*) 0
PhCMe ‖ NP(O)Ph_2		Na Li	78(*R*) 30(*R*)
PhCO-*i*-Pr		Na	73(*S*)
PhCO-*i*-Pr		—	7(*S*)
PhCO-*i*-Pr		Na	76(*R*)
PhCO-*i*-Pr		—	36(*R*)

As evident from the table, the product ee values are consistent with this series: the less perfect C_2 symmetry of the complex, the higher the ee value.

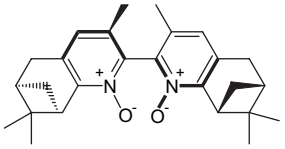
The relationship between the reaction enantioselectivity and the C_1, C_2 symmetry of a chiral catalyst is not limited to catalytic and stoichiometric reactions with the participation of metal complexes. This effect becomes apparent on some reactions over chiral organocatalysts. For example, Lewis-basic C_1 and C_2 chiral *N*-oxides **287** and **288** have different enantioselectivity as catalysts in the allylation of aldehydes:[294]



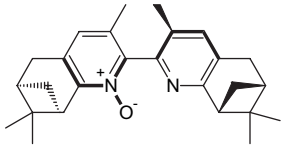
(16)



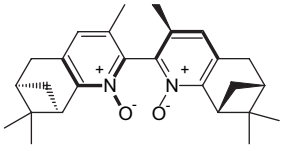
C_1-(*Ra*)-**287**, 98(*S*)



C_2-(+)-**288**, 14(*R*)



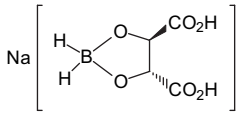
C_1-(*Sa*)-**287**, 82(*R*)



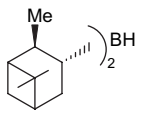
C_2-(–)-**288**, 10(*S*)

It can be seen that the C_1 and C_2 symmetry of the chiral organocatalysts strongly affects the ee values of reaction 16 product.

The results of acetophenone reduction by chiral C_2- and C_1-boronic esters or organoboranes can be interpreted analogously (Table 13).



289



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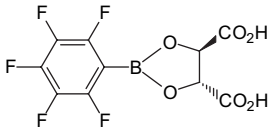

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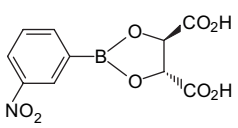

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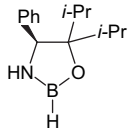
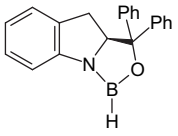
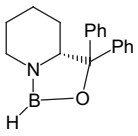


293



294



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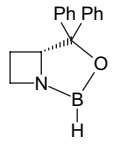


296

Indeed, the transition from C_2 **289**–**291** to C_1 **292**–**296** chiral auxiliaries leads to a positive leap in enantioselectivity.

The influence of C_2–C_1 symmetry of chiral auxiliaries on enantioselectivity in a stoichiometric reaction of the abovementioned types is evidence in favour of an assumption that this effect is not confined to catalytic reactions or reactions involving metal complexes. It seems that this effect could be explained on the basis of the symmetry of intermediate complexes responsible for asymmetric induction.

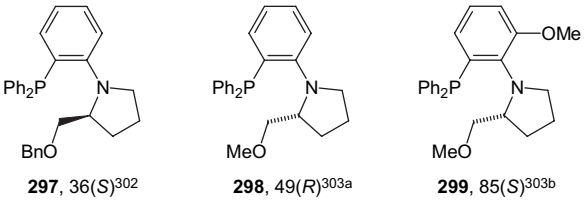
Table 13
Reduction of acetophenone with chiral C_2- and C_1-boronic esters and organoboranes

Boronic ester or organoborane	Symmetry	*T* (°C)	ee [%] (config. of 1-phenylethanol)	Ref.
289	C_2	rt	0–0.2	295
290	C_2	0	9–14(*R*)	296
291+$LiBH_4$	C_2	rt	13(*R*)	297
292+$LiBH_4$	C_1	rt	99(*R*)	297
293	C_1	30	94(*R*)	298
294	C_1	30	93(*R*)	299
295	C_1	0	87(*S*)	300
296	C_1	0	95(*S*)	301

10. C_2, C_1 Configurational models

The enantioselectivity is provided by the spatial fixation of bulky groups of the ligand nearest to the donor atoms forming

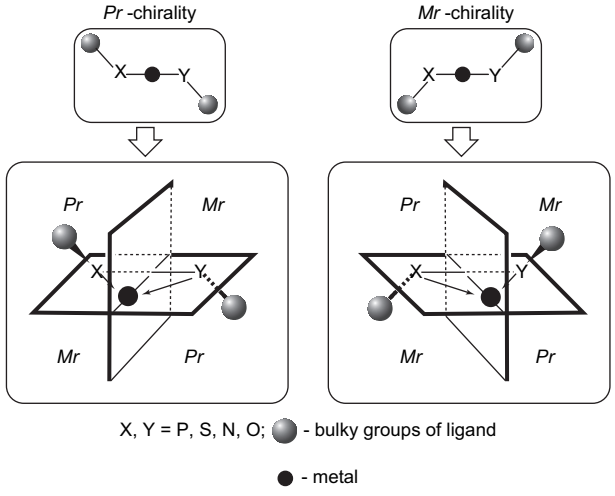
the metal atom chiral environment. In other words, the ligand molecule within a catalytic complex plays the role of a template. There is a good reason to believe that the reaction enantioselectivity depends on real coordinates of ligand substituents and their chiral array around the metal atom of a complex as catalysts. For example, ligands **297**–**302** have a chiral centre in the *N*-ring that can rotate around the C–N bond. Only two ligands (**299** and **302**) include substituents preventing free rotation. It is exactly these ligands of Pd complexes that cause a sharp increase in enantioselectivity of reaction 3. The product gains high ee values if a stable and rigid position of the chiral centre in the ligands **299** and **302** is ensured.[302,303]



297, 36(*S*)[302] **298**, 49(*R*)[303a] **299**, 85(*S*)[303b]

300, 24(*R*)[303a] **301**, 35(*R*)[303a] **302**, 74(*R*)[303a]

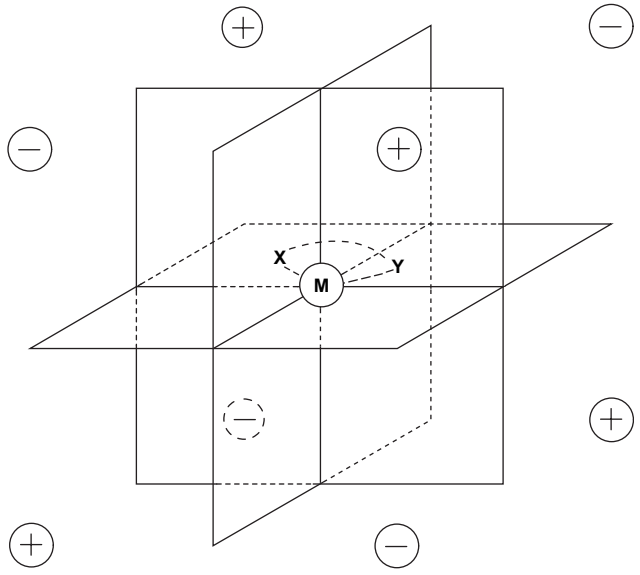
Thus, it is only possible to predict both the product configuration and ee values if precise spatial coordinates of bulky groups that form the metal atom chiral environment under the reaction conditions are known. An attempt has been made to forecast enantioselectivity parameters on the basis of a configurational model of the complex location in the quadrant volume[304] (Scheme 5).



Scheme 5.

The regions determining complex chirality are marked with indices *Pr* (plus region) and *Mr* (minus region); the reaction product configuration depends on the region *Pr* or *Mr* where the ligand fragments fall. This model has found experimental support in the *Mr*-(*R*) and *Pr*-(*S*) dependence observed in allylic alkylation of 1,3-diphenylprop-2-enyl acetate by the diethyl malonate anion on palladium complexes with iminophosphine, diphosphine and diamine ligands.[304a]

The space in front of and behind the metal atom has not been differentiated in this model (see Scheme 5). This constrains the *Pr*/*Mr* model, because the *Pr* (or *Mr*) space in front of and behind the metal atom has a different chirality sign.[6a] The octant projection with the metal atom in the centre and with different signs of the front and back octants is devoid of this limitation[6a] (Scheme 6). A comparison of the configurational models *Pr*/*Mr* and Pr^{oct}/Mr^{oct} in several reactions demonstrated that the Pr^{oct}/Mr^{oct} model is more appropriate for the experimentally determined enantioselectivity of some reactions.[6a]



$Mr^{oct.}$ (Minus region octants)
FL(–)(front left — (–)); FR(–)(front right — (–));
BL(–)(back left — (–)); BR(–)(back right — (–));
$Pr^{oct.}$ (Minus region octants)
FL(+)(front left — (+)); FR(–)(front right — (+));
BL(+)(back left — (+)); BR(–)(back right — (+));

Scheme 6.

Unfortunately, X-ray diffraction data, e.g., of transition metal chelate complexes[305] as catalysts of reactions in solutions, can hardly be used as a reliable basis in the construction of quantitative models of the structural elements of the complex—ee and product configuration type. Equalization of the molecular parameters of complexes in the crystal to those in solution is probably unjustified. However, this approach gives positive results when using relative values, such as changes in certain complex parameters due to the presence of ligands with similar structures. Thus, it has been found[306] that, in the case of an asymmetric Diels–Alder reaction, where acrylates react with cyclopentadiene in the presence of the Ti-2,2′-biaryldiol complex, a dependence of ee of the *endo*-adduct on the biaryl torsion angle passes through a maximum. A similar

dependence exists between ee and the calculated parameter, chirality content of molecule (CCM), used as a quantitative measure of chirality of the given chiraphore[¶] (in the case of the biaryl fragment).[307] Correspondingly, a linear dependence exists between the CCM and dihedral angles. This testifies to the non-linear dependence between CCM and the experimental ee value of the reaction product.[307] Most probably, the introduction of the parameter CCM[308] opens up a new way for predicting the enantioselectivity magnitude and sign on the basis of calculations.

A majority of quantitative theoretical approaches dealing with asymmetric homogeneous catalytic reactions catalyzed by metal complexes are based on computations that employ different programmes and methods for different reactions and catalysts. The conformity of the calculated parameters with the experimental data is considered to be evidence in favour of the suggested mechanism. Recently, calculations have been carried out for enamide hydrogenation in the presence of the Rh-**9** complex,[309] for hydrogen transfer hydrogenation of ketones catalyzed by Rh-diamine,[110,310] Ru–*N*-tosylethylenediamine[311] or Ru-amino alcohol complexes,[142a,311,312] and for cyclopropanation of styrene on the complex Cu–*N*,*N*′-dimethylmalonaldiimine,[313] etc.

Although the use of the configurational models *Pr*/*Mr* or Pr^{oct}/Mr^{oct} is a qualitative approach, it provides a simple tool for predicting the asymmetric induction sign and its interpretation.

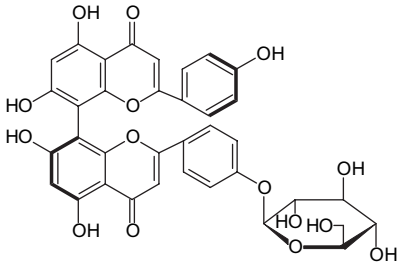
It is of note that the interpretation of the effects of metal complexes on enantioselectivity in catalytic reactions using the models Pr^{oct}/Mr^{oct} or *Pr*/*Mr* is based on static factors. These effects are steric in nature. An alternative explanation based on dynamic factors also exists. A recently proposed theory[314,315] of the chiral molecular recognition and induction is based on helical electronic effects in a chiral metallocomplex (catalyst) and coordinating substrate. Handedness matching of the sign of helical polarizability of a chiral catalyst and a coordinating substrate in enantioselective reactions should be implemented.

11. C_2, C_1 Symmetry of chiral molecules in bioorganic chemistry

As seen from the experimental data review, there are two groups of reactions on metal complexes distinguished by efficiency of C_2-symmetric chiral auxiliaries. Reactions of the first group proceed with a high enantioselectivity degree in the presence of C_2 chiral ligands. Strange as it may seem, some reactions on metal complexes with C_2-symmetric chiral ligands are not inferior to bioreactions neither in enantioselectivity nor in conversion. For example, hydrogenation of β-ketoesters over a Ru catalyst with C_2-symmetric atropoisomeric chiral ligands proceeds with 100% conversion and 99.9% ee values of the product.[316] Bioreduction of this substrate occurs with conversion and enantioselectivity: 91%, 95% ee;[317] 68%, 99% ee;[318] 85%, 100% ee,[319] correspondingly, in the presence of carbonyl reductase of different types.

Hence, C_2-symmetric chiral metal complexes, as catalysts of this reaction, are emulating enzymes. Chiral metal complexes, as catalysts, have some common features with enzymes such as high enantioselectivity, very significant turnover[‖] and covalent interaction between the catalyst and substrate in the transition state.[320] However, nature has selected a way that excludes the use of C_2-symmetric chiral auxiliaries as ligands (enzyme side chains).[**] The DNA linear polymer consists of four nucleotides in an irregular sequence as a foundation of the genetic variety. Two DNA molecules form a double helix by H-bonding of complementary nucleotides. Both helices and an α-helix of natural peptides have a *P* configuration. The structures of all helices are asymmetric.[322]

Only L-amino acids are constituents of proteins and only D-nucleotides are incorporated in nucleic acids. Polysaccharides are also built from D-monosaccharides (with rare exceptions). All these substances are C_1-symmetric chiral (asymmetric). These enantiomers are the same in living systems of the human race, animals, plants and microorganisms.[323] C_2-Symmetric chiral compounds are extremely rare in nature. The question is whether this natural selection is associated with a difference between C_1- and C_2-symmetric chiral auxiliaries in some reactions. The most well known is D-(+)-tartaric acid that represents a by-product of grape juice alcoholic fermentation. A well-known C_2 chiral natural molecule is the alkaloid, (−)-sparteine.[324] There are, at most, ~10–20 C_2-symmetric chiral alkaloids from a few thousand alkaloids, many of which are optically active.[325] There are known several C_2 chiral lignans.[326–328] All these substances are rather by-products than main products of plant metabolism. Sometimes, asymmetric molecules occur in nature with bulky C_2-symmetric chiral fragments.



303

An example of such a structure is cupressuflavone glucoside **303** isolated from *Juniperus communis* var. *depressa*.[329] Thus, C_2-symmetric chiral compounds do not participate in important chemical reactions of life-support systems.

12. C_3 Chiral auxiliaries

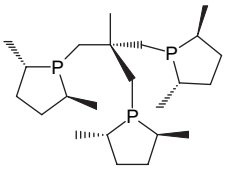
It has been reported[330] that chiral recognition in host–guest complexation by C_3- and D_3-symmetric receptors, which was

[¶] By analogy with the terms 'chromophore' and 'pharmacophore'.

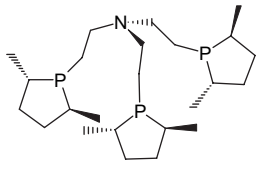
[‖] We[162] have observed that hydrogenation of methyl acetoacetate on the complex [RuCl(η⁶-*p*-cymene)((*R*)-**13**)]Cl occurs with high enantioselectivity and conversion at molar ratio substrate/catalyst 70,000.

[**] Biomacromolecules carry out enantioselective transformations using even achiral or racemic metal complex catalysts,[321] let alone C_2 or C_1 chiral metal catalysts.

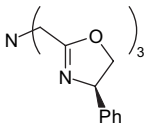
examined on Newman projections should be poor or just zero. This may also be the reason why a successful differentiation of enantiomers by D_3-crown ethers has not been observed until now.[330,331] The opposite point of view[332] is based on an inspection of the same stereoprojections along the C_3-axis. However, the problem, as applied to asymmetric catalysis, is not only in the differentiation of the enantiotopic sides of a substrate by a C_3 receptor (catalyst), but also in the stereochemical possibility of a substrate attack along the C_3-axis. The most prominent examples of successful C_3-ligands are listed below



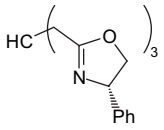
304 (*ee* = 89)[333]



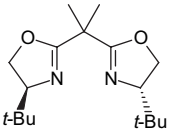
305



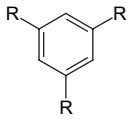
306 (*ee* = 69–88)[334]

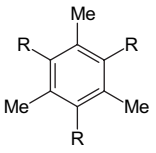


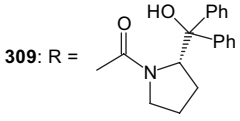
307 (*ee* = 87)[335]



308 (*ee* = 70–80)[336]

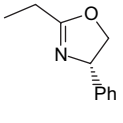






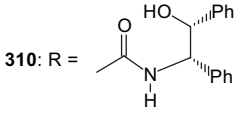
309: R =

(*ee* = 96)[337]



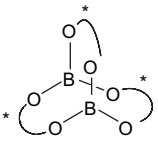
311: R =

(*ee* = 13)[339]



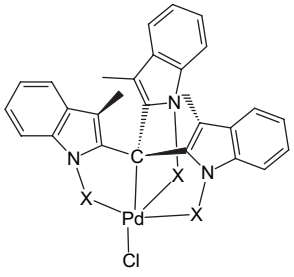
310: R =

(*ee* = 92)[338]



312: =(R)-**35**

(*ee* = 90)[340]



313: X = PPh_2

(*ee* = 7)[341]

(enantioselectivity data are given for the reactions which follow).[333–339] C_3 Receptors **304**–**307** and **309**–**313** have chiral fragments in their side chains, which can be coordinated as mono-, bi- or tridentate chiral ligands. It has been shown by X-ray spectroscopy that the complexes [Rh(COD)(**304**)]SbF_6 and [Rh(CO)(**305**)]Cl in the crystal have trigonal bipyramidal structures with a C_3 symmetry axis along the Rh–CH and N–Rh–CO bonds, respectively.[333] The former complex has been used as a catalyst precursor for the hydrogenation of methyl (*Z*)-α-acetamidocinnamate with an ee of the product of 89%. However, a rhodium complex with the C_2-bidentate R–CH_2–CH_2–R ligand **7**, where R is an analogous phosphane cycle, catalyzes the hydrogenation of a similar substrate with ee= 98%.[10] The mechanism of this reaction on Rh/C_2-ligands has been studied by the groups of Halpern, Brown and Imamoto (see review in Ref. 6b). It has been shown that the metal atom of the catalytic precursors lost C_2 central symmetry in the intermediate complexes responsible for asymmetric induction. Asymmetric induction occurs in the octahedral dihydride intermediate of Rh(III) with a bidentate ligand and enamide as substrate, which is coordinated by two metal atom vacancies. Therefore, the C_3-ligand can be occupied only by two vacancies of the intermediate. The central metal atom in the important octahedral intermediate loses the C_3 symmetry axis, even though the C_3-ligand occupies three coordinational vacancies. In this case, asymmetric induction also occurs in the intermediate complex with C_1 symmetry of the central atom. Thus, the above-mentioned experiment cannot be considered as undeniable evidence of the enantioselective action of C_3 auxiliaries in this reaction. Copper complexes with oxazolinyl auxiliaries **306**[334] and **307**[335] are also effective catalysts in the asymmetric reaction of allylic oxidation.

The possibility that C_3 auxiliaries are coordinated in the intermediate complex of this reaction with only two side chains is also high. Indeed, the same copper complex with C_2-symmetric oxazolinyl ligand **308** catalyzes this reaction with relatively similar ee values. The possibility of C_3-ligand coordination with two vacancies retains its validity in the reactions listed below. Diethylzinc addition to aromatic aldehydes in the presence of oxazolinyl C_3-ligands of the type **306**, **307** and **311** occurs with good enantioselectivity (ee up to 90%).[342] Prochiral ketone reduction proceeds very enantioselectively on the C_3 borane complex with β-hydroxy amide **309**.[337] Alkynylation of aromatic aldehydes occurs with high enantioselectivity on the Ti(O-*i*-Pr)$_4$/**310**[338] complex. The side chains of auxiliaries **309** and **310** can be used as chiral bidentate ligands. In this case, there are possibilities of coordination of the side chain alone as the C_1 auxiliary. If the bidentate function of the side chains is lost, as in **311**, the reaction enantioselectivity is decreased. For example, enantiomeric recognition of substrates of the α-phenylethylammonium ion type with **311** takes place with small enantioselectivity (up to 71(*R*):29(*S*)).[339]

Very high enantioselectivity has been achieved in Diels–Alder reactions over borate propeller compound **312**.[340] If the side chains lose chirality centres and enantioselectivity is responsible for the chiral C_3 receptor only, as in **313**, rather low ee values of the product of a cross-coupling reaction

have been observed.[341] It seems that the problem of using C_3 receptors needs further investigations from a conceptual point of view.

Strange as it may seem, C_3-symmetric chiral molecules are encountered in living systems (see review in Ref. 343). However, their functions are limited basically by ion transport. There are synthetic C_3-symmetric molecules,[343,344] which mimic biological functions. It is doubtful if these molecules act as true C_3 receptors because of their huge molecular sizes.[344]

13. Conclusions

In this report, an analysis of the experimental data in the field of asymmetric reactions on C_2- and C_1-symmetric chiral metal complexes as catalysts has been undertaken. It may be concluded that the ee values of the reaction products are dependent on the C_1 or C_2 symmetry of the intermediate complexes responsible for asymmetric induction in these reactions. If the intermediate complex responsible for asymmetric induction is chiral, C_1-symmetric (asymmetric), the reaction can be carried out with a high enantioselectivity level, irrespective of the symmetry of the starting chiral auxiliaries. Among the reactions of this type discussed in the report are hydrogenation of α-acetamidocinnamic acid, hydrogenation of unfunctionalized olefins and ketones on Ti, Zr and Sm complexes, hydrosilylation of acetophenone by diphenylsilane, allylic alkylation of 1,3-diphenyl-2-propenyl acetate by dimethyl malonate sodium salt, cyclopropanation of styrene with α-diazoacetate, hetero-Diels–Alder reactions of Danishefsky's dienes with aldehydes, alkylation of benzaldehydes with diethylzinc in the presence of the Ti(O-*i*-Pr)$_4$ complex and allylation of aldehydes.

If the intermediates responsible for asymmetric induction in the reactions retain the symmetry of the starting chiral auxiliaries, those reactions on complexes with C_1-ligands have high enantioselectivity, as compared to C_2-ligands. From the observed catalytic reactions, alkylation of benzaldehyde with diethylzinc (without Ti(O-*i*-Pr)$_4$), hydrogen transfer hydrogenation of acetophenone, hydrogenation of ketopantoyllactone, hydrogenation of acetophenone and unfunctionalized alkenes on Rh and Ir complexes, hydroformylation of styrene, conjugate addition of diethylzinc to chalcone and stoichiometric reactions with the participation of metal complexes fall within the second group.

In evaluating the dependence of the reaction enantioselectivity on the ligand symmetry, it should be taken into account that the differences in structural or electronic factors of the ligands as well as the reaction conditions are superior to C_2 and C_1 symmetry distinctions. Nevertheless, some regular trends can be observed, even with a formal approach to the evaluation of the C_1 and C_2 symmetry influence on enantioselectivity, because this approach is based on a comparison of a great number of diversified ligands in closely parallel circumstances (reactions, metal catalysts, substrates and reaction conditions are identical).

It should also be emphasized that a degree of the C_2 symmetry influence of the starting chiral auxiliaries of the second group reactions on enantioselectivity depends on the symmetry quality. The smaller the possible divergence from the ideal C_2 symmetry, the smaller the enantioselectivity. For example, the enantioselectivity of oxidation of sulfides by hydroperoxides in the presence of Ti(O-*i*-Pr)$_4$/L* (Table 11) ranges from 0 to 89–99% ee in accordance with the quality of C_2 symmetry of the ligands. Reaction 10 involving ideal C_2-symmetric Rh complexes with the ligands **230–232** proceeds with zero enantioselectivity. Alternatively, an increase in enantioselectivity of this reaction can be explained by a possible divergence from the ideal C_2 symmetry. The analogous symmetry dependence is observed in the reduction of acetophenone by chiral hydrides (Table 12).

In accordance with the reviewed data, it is possible to assume that the term asymmetry is more acceptable and uniform as applied to the phenomenon of asymmetric induction of a chemical reaction. The use of chiral induction instead of asymmetric induction in recent publications (see Ref. 345) is probably not an innovation.

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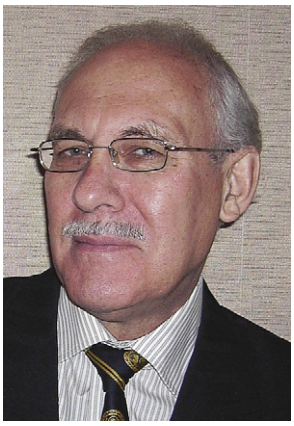
Biographical sketch



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