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The central chirality of the metal atom and configurational relations in asymmetric reactions catalysed by metal complexes †

V A Pavlov

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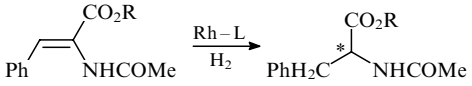
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Abstract. The recently published data on the dependence of the configuration of the reaction product on the structure of a catalytic metal complex (or an intermediate determining the asymmetric induction) in asymmetric catalytic reactions of hydrogen-transfer hydrogenation of acetophenone, hydroformylation of styrene, allylic alkylation of 1,3-diphenylprop-2-enyl acetate and alkylation of benzaldehyde with dialkylzinc are systematised. The applicabilities of octant and quadrant projections of the complexes are compared in order to establish the relationships between their structures and the enantioselectivities of the reactions. The known mechanisms of asymmetric induction in these reactions are discussed with regard to the C_1 or C_2 symmetry of the catalytic complex. The reasons for a decrease in the enantioselectivities of hydrogen-transfer hydrogenation, hydroformylation and alkylation by dialkylzinc [in the absence of $Ti(OPr^i)_4$] when performed with complexes with chiral C_2-symmetric ligands (as compared with complexes with asymmetric ligands) are considered. The bibliography includes 435 references.

I. Introduction

Asymmetric catalysis is undergoing a period of explosive development as can be evidenced from the increasing number of publications (see the monographs [1–5] and the most recent reviews [6–23]) and financial support of this field of research. The interest of the pharmaceutical industry in asymmetric catalysis stems from its possible use for the preparation of enantiomerically pure drug components. In 1996 – 1998, the annual expenditures for their production increased from US $ 73 bln to 96 bln.[24] The number of publications devoted to the theoretical aspects of asymmetric homogeneous catalysis was steadily increased correspondingly.

Studies into the mechanisms of asymmetric reactions on metal-complex catalysts that yield products with great enantiomeric excess (*ee*) attract special attention. The hydrogenation of enamides of α-acetamidocinnamic acid derivatives, on rhodium phosphine complexes is especially well-studied.[6]



In the 1980's, following a publication by Galpern and Brown (for Ref. 6), it was thought that the predominant mechanism of this reaction is characterised by the following features:

(1) the first reaction step yields two intermediate complexes with the substrate, *viz*., minor and major, the concentration of the former being order of magnitude lower than that of the latter;

(2) the asymmetric induction occurs in the subsequent transformation of the intermediate;

(3) the major enantiomeric product is formed predominantly *via* the minor intermediate, since the rate of its reaction exceeds that *via* the major intermediate by three orders of magnitude.

However, a recently postulated alternative mechanism [25, 26] entails the formation of a hydride complex in the first step, the asymmetric induction as a result of substrate coordination and the formation of the predominant enantiomer of the reaction product *via* the major intermediate.

This discussion is not yet complete, since both mechanisms of reactions on rhodium [27, 28] and ruthenium complexes [28, 29] have advocates of their own. Presumably, the reaction mechanism depends on the nature of the catalytic complex with different phosphine ligands. However, the similarity of the dependences of the product configuration on the structure of the catalytic complex [10] (see Section II) is rather in favour of a single mechanism.

The character of the asymmetric induction step is the key difference between the aforesaid mechanisms. However, even if the asymmetric induction occurs in different reaction steps, this does not always account for the differences in the configurations of the reaction products. The dependence mentioned above is consistent with either mechanism on the assumption of a random coincidence of the product configuration in the case of one or another asymmetric induction step. Formally, only the second mechanism fits well into the most popular concept on the interaction of a chiral complex with a substrate commonly

V A Pavlov N D Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp. 47, 119991 Moscow, Russian Federation. Fax (7-095) 135 53 28. Tel. (7-095) 938 35 02.
E-mail: pvlv@cacr.ioc.ac.ru

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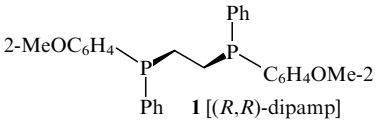
† Dedicated to the memory of Prof. G Snatzke.

known as a 'key–lock' mechanism. The overwhelming majority of configurational models used in asymmetric homogeneous catalysis also fit into this model.

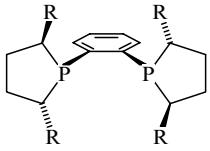
The construction of configurational models, *i.e.*, determination of simple relationships between the configurations of asymmetric catalystic reaction products and those of chiral metal complexes that play the role of the catalysts attracts special attention.

II. Configurational models in asymmetric homogeneous catalysis

Knowles [30] who studied the hydrogenation of α-acetamidoacrylic acid in the presence of the Rh–dipamp complex (**1**) recommended that the so-called quadrant diagram was used to determine the efficient and non-efficient coordination variants of an enamide in a hypothetical transition complex.[6, 10]

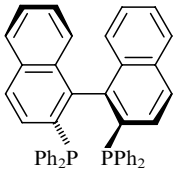


1 [(*R*,*R*)-dipamp]



2 [(*R*,*R*)-duphos]

R = Me, Et, Pr^n.



3 [(*R*)-binap]

This diagram is based on the arrangement of the phosphine phenyl groups (with the edge or the plane facing the viewer) in the precursor of the catalytic complex as established by X-ray diffraction spectroscopy. [31] According to this diagram, the substituents of a coordinated substrate that fall into the quadrants blocked by the phenyl groups of the ligand turned edgewise to the viewer encounter with a greater steric hindrance. A similar diagram with two blocked diagonal quadrants (Fig. 1) was used by Burk *et al.*[11, 32, 33] to rationalise the enantioselectivity of enamide hydrogenation in the presence of the Rh–duphos complex (**2**). The results of computations based on this model [27] were in good agreement with the experimental data.

A similar graphical approach based on a sector diagram was developed for the consideration of hydrogenation of β-keto esters,[34, 35] β-keto sulfonates [36] and other β-keto derivatives [7] on the Ru–binap complex (**3**).[10] Whereas the Ru–(*R*)-binap complex catalyses the formation of *R*-alcohols, the Ru–(*S*)-binap complex favours the formation of *S*-hydroxy derivatives. Pfaltz *et al.*[37–39] used a projection of a catalytic complex and a substrate coordinated by this complex, which is similar to the quadrant projection, to establish the preferential coordination of the substrate and, correspondingly, the configuration of the product formed upon reduction of α,β-unsaturated esters and amides with sodium cyanoborohydride in the presence of an *in situ* generated complex $CoCl_2$–**4**.

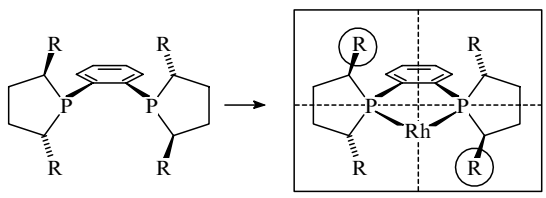
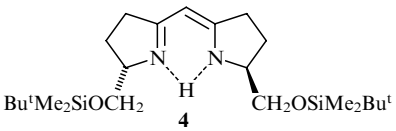


Figure 1. Shielding of diagonal quadrants in a rhodium complex with (*R*,*R*)-duphos in the hydrogenation of enamides.[11, 32]



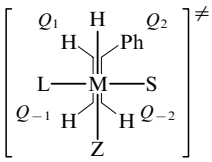
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The transition-state model [40] of yet another popular asymmetric reaction, *viz.*, hydroformylation on rhodium and palladium complexes (Section IV), is based on the quadrant projection of a chiral complex. Within the framework of this model, asymmetric induction takes place in the substrate coordination step as is tacitly accepted for other intermediates mentioned above. This model is based on the following assumptions:

(1) an activated complex resulting in the formation of a metal–alkenyl intermediate possesses the highest free energy;

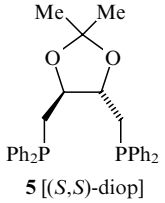
(2) in the transitions state, the double bond of the substrate is approximately coplanar with the bond between the metal and hydrogen.

The transition state is displayed as a projection of a complex onto a plane perpendicular to the direction of approach of the substrate to the metal atom. The ligands L and S and the reagent Z differ in size: L > S, Z > H (*e.g.*, Z = CO). The metal–ligand bonds form quadrants differing in the degree of occupation of space with these ligand fragments. The four variants of the distribution patterns of substrate substituents between the quadrants depending on substrate orientation correspond to four intermediate states characterised by different values of free activation energies (Q). The predominant orientation of styrene shown in the scheme corresponds to the arrangement of the ligands and the ratios of Q.

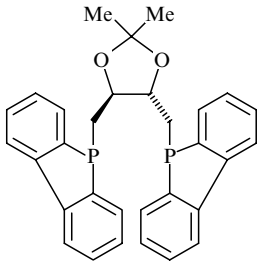


M is metal, $Q_{-1} > Q_{-2} \gg Q_1 > Q_2$.

The distribution of the molecular masses of the ligands between the quandrants, especially for C_2-symmetric bidentate ligands, such as diop (**5**) and dbp-diop (**6**), for which this model has been constructed (for rhodium [40–42] and platinum [41, 43–45] complexes), remains unclear.



5 [(*S*,*S*)-diop]



6 [(*S*,*S*)-dbp-diop]

Besides, this model does not take into account the fact that the enantiomeric outcome of the reactions carried out on rhodium and platinum catalysts can be different even if the same ligands are used.[41, 46] The experimental proof of this model showed that the predicted isomeric compositions of the reaction products and the configuration of the chiral product do not often coincide with the experimental data.[47] This fact was also acknowledged by the authors.[40, 41]

In practice, the relative positions of the ligands L and S in the transition state are deduced from the results of hydroformylation of a simple substrate;[47] therefore, the model under consideration is more explanatory than predictive.

A combination of quantum-chemical calculations and the molecular mechanics method was used in the construction of yet

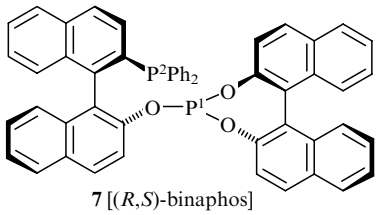
another semiquantitative model of this reaction.[48] Experimental data suggest a trigonal-bipyramidal structure of an intermediate with a coordinated alkene.[49] The admissions underlying this model are very similar to those used in the previous model:

(1) the double bond of the substrate is coplanar with the apical bond M – H;

(2) the substrate coordination step is responsible for the regioselectivity and enantioselectivity;

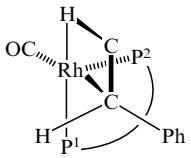
(3) this step is irreversible.

It has previously been established [48] that this model provides an adequate interpretation of the data on hydroformylation of alkenes in the presence of the Rh – (*R*,*S*)-binaphos complex (**7**).[49]

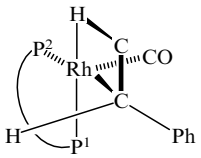


7 [(*R*,*S*)-binaphos]

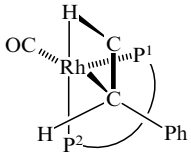
With styrene as a substrate, four intermediates (**A** – **D**) are possible.



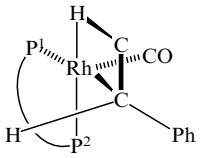
A



B



C

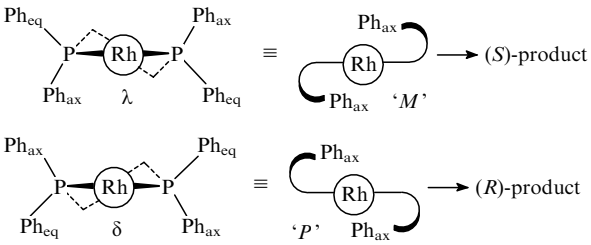


D

The coincidence of the calculated value of *ee* and the product configuration with the experimental results is achieved only with the intermediate **A**. A drawback of this model is that another intermediate can be more preferable for ligands having different structures. The calculated data should be compared each time with the experimental results; hence, this model also has a limited predictive potential.

Simpler literal rules for the dependence of the product configuration on the complex structure have been proposed. The relationship between the configurations of the enamide hydrogenation products and the conformations of the five-membered chelate rings in the rhodium complexes with bis(diphenylphosphine) ligands were simultaneously and independently established by Kagan [50] and by Pavlov and Klabunovskii.[51 – 53]

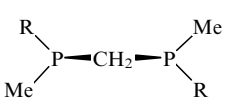
In this case, the folded conformations, λ and δ, were formed due to the presence, in the ring, of bulky substituents at one or two chiral carbon atoms. The conformation λ of the chelate ring results in (*S*)-, whereas the conformation δ yields the (*R*)-enantiomer of the reaction product.



This model was further extended to rhodium complexes used for enamide hydrogenation with seven-membered chelate rings in the λ-twist-chair and δ-twist-chair conformations.[10, 52 – 56] Similar dependences were found for hydrosilylation,[10, 55] cross-coupling [10, 57, 58] and allylic alkylation [59] on Rh, Ni, Pd, *etc.* complexes.

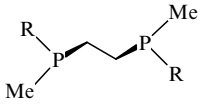
As the enantioselectivity of this reaction is directly related not to the conformation, but rather to the chiral arrangement of the phosphine phenyl groups determined by this conformation,[60, 61] a more general expression for the same dependence which is based on a conventionalised image of a helix loop can be used.‡ In this case, the indices '*P*' and '*M*' describe the chiral arrangement of molecular masses of two pairs of phosphine phenyl groups in the complex.

For simplicity's sake, this regularity can be described by the dependence [10] λ('*M*') – (*S*), δ('*P*') – (*R*). Obviously, it is the use of '*P*'/'*M*'-indices only that is applicable in the case of enamide hydrogenation on rhodium phosphine complexes where the chirality of the ligands is determined either by the chiral phosphorus atoms [(*R* ,*R*)-miniphos (**8**),[62] (*R*,*R*)-bisP* (**9**) [63]] or by four chiral carbon atoms located pairwise in two rings containing phosphorus atoms [(*S*,*S*)-bpe (**10**), (*R*,*R*)-**2**].[32]



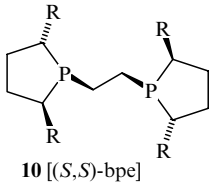
8 [(*R*,*R*)-miniphos]

R = Pr^i, Bu^t, cyclo-C_6H_{11}, Ph.



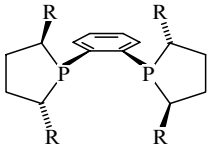
9 [(*R*,*R*)-bisP*]

R = Bu^t, Et_3C, 1-adamantyl, *etc.*

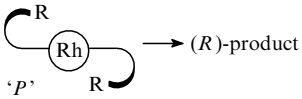


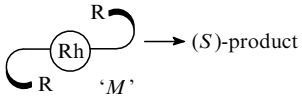
10 [(*S*,*S*)-bpe]

R = Me, Et, Pr^n, Pr^i.



2 (R = Me, Et, Pr^n).





In the case of rhodium complexes with the ligands **8** and **9**, the indices are given with respect to substituents R bulkier than the methyl group, whereas those for the complexes with ligands **10** and **2** are determined from the substituents facing the viewer.

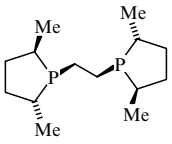
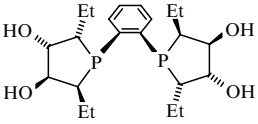
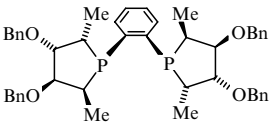
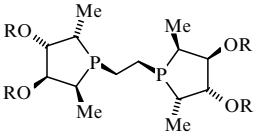
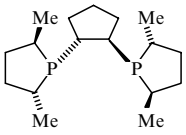
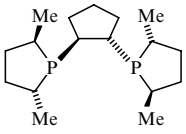
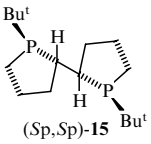
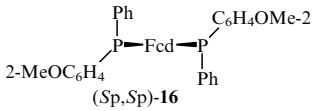
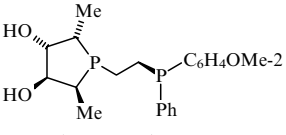
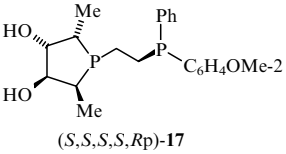
Hydrogenation of methyl α-acetamidocinnamate in the presence of the rhodium complexes with the ligands **10** – **17** and **1** obeys the regularity '*M*' – (*S*), '*P*' – (*R*) (Table 1). Thus, this concept may have a predictive potential.

The enantioselectivities of the hydrogenation reactions of α-acetamidocinnamic acid derivatives in the presence of the complexes Rh – **2**,[32] Rh – **10** and Rh – (**11** – **13**) are virtually the same. Thus, additional chiral carbon atoms in the ligand more remote from the metal atom in the chelate complex than the carbon atoms in the substituents that determine the chirality in the quadrant projection, have no effect on the enantiodiscrimination. The change in the configuration of the chiral donor phosphorus atom in the 'hybrid' ligand **17** has a much more pronounced effect on the value (but not the sign) of the enantioselectivity.

In total, more than 80 structural variants of chiral ligands [10] involved in the hydrogenation of enamides on rhodium complexes have been considered. All of them (with the exception of several deviations which have a specific explanation of their own) obey the above-mentioned regularity. Unfortunately, the involvement of a rhodium complex containing a cyclophane bis(diphenylphos-

‡ Quotation marks are used in this case to denote the helicity indices.

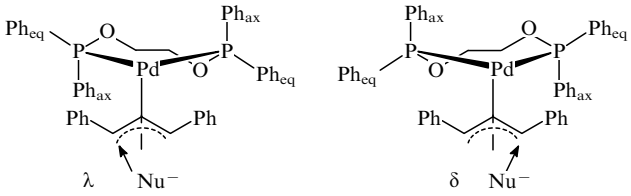
Table 1. Hydrogenation of methyl α-acetamidocinnamate in the presence of Rh complexes with the ligands **10** – **17**.

Ligand	Chirality indices	Product configuration	*ee* (%)	Ref.
 **10** [(*R*,*R*)-bpe]	'*P*'	*R*	98	32
 (*S*,*S*,*S*,*S*)-**11**	'*M*'	*S*	> 99	64
 (*S*,*S*,*S*,*S*)-**12**	'*M*'	*S*	96	65
 (*S*,*S*,*S*,*S*)-**13** (R = Bu^t, Bn)	'*M*'	*S*	~98	65
 [λ-(*R*,*R*)]-**14**	'*P*'	*R*	73	66
 [δ-(*R*,*R*)]-**14**	'*P*'	*R*	95	66
 (*S*p,*S*p)-**15**	'*P*'	*R*	> 99	67
(*R*p,*R*p)-**1**	'*M*'	*S*	94	31
 (*S*p,*S*p)-**16**	'*P*'	*R*	96	68
 (*S*,*S*,*S*,*S*,*S*p)-**17**	'*M*'/'*P*'	*S*	43	69
 (*S*,*S*,*S*,*S*,*R*p)-**17**	'*M*'	*S*	92	69

Note. Hereinafter Fcd is ferrocenylene.

phine) ligand with planar chirality [70] cannot adequately be analysed due to the lack of X-ray diffraction data.

A model of configurational relationships based on the conformations of the intermediates was employed in the study of allylic alkylation products of 1,3-diphenylprop-2-enyl acetate (Section V) by a diethyl malonate anion in the presence of a bis(diphenylphosphinite) palladium complex.[59, 71]

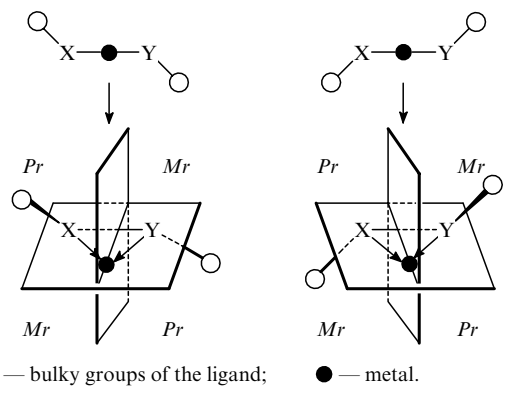


It was found that the λ-conformation of the intermediate favours the formation of the *S*-product, whereas the δ-conformation yields the *R*-enantiomer.

A more general configurational model considers the arrangement of the complex in the space of the quadrant (Fig. 2).[72, 73]

The regions determining the complex chirality are marked by the indices *Pr* (plus region) and *Mr* (minus region); the configuration of the reaction product depends on the region *Pr* or *Mr* where the ligand fragments fall. This model has found experimental support in that the dependence *Mr* – (*R*), *Pr* – (*S*) was observed in the allylic alkylation of 1,3-diphenylprop-2-enyl acetate by a diethyl malonate anion catalysed by palladium complexes with iminophosphine, diphosphine and diamine ligands.[72] However, the choice of this reaction is not quite suitable. In terms of this model, the asymmetric induction occurs in the substrate coordination step (the 'key – lock'-type interaction). However, the asymmetric induction step of this reaction does not coincide with the substrate coordination step (see Section V). Therefore, this model is applicable to such reactions as ketone hydrogen-transfer hydrogenation and to certain enamide hydrogenation, ketone hydrosilylation reactions, *etc*., where the asymmetric induction occurs in the substrate coordination.[6] A drawback of this model is that the space in front of the metal atom is not taken into consideration. The model is inapplicable to complexes with ligands, the bulky fragments of which face the viewer (see Fig. 2) and are nearer to it than the metal atom. Indeed, the complexes with ligands **18** and **19**, **20** and **21** (see Table 2) possess different *Pr*/*Mr*-chiralities, but the configuration of the allylic alkylation product of 1,3-diphenylprop-2-enyl acetate by a diethyl malonate anion is similar in these pairs.§ As a matter of fact, two phenyl groups in the

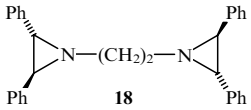
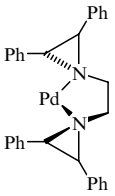
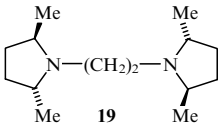
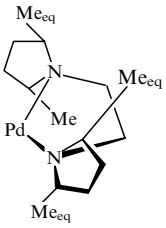
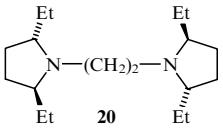
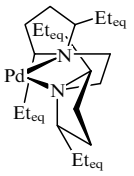
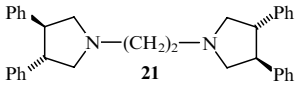
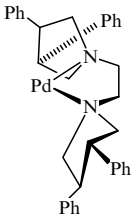
§ The conformations employed in the construction of complexes using molecular models corresponded to more favourable equatorial positions of bulky substituents in the chelate rings.[76, 77]



○ — bulky groups of the ligand; ● — metal.

Figure 2. A configurational model of the location of a complex in the quandrant volume.[72, 73]
(*a*) *Pr*-chirality, (*b*) *Mr*-chirality; X, Y = P, S, N.

Table 2. Comparison of the configurational models *Pr*/*Mr* and Pr^{oct}/Mr^{oct} in the allylic alkylation of 1,3-diphenylprop-2-enyl acetate by diethyl malonate anion under the action of palladium complexes with diamines.[74, 75]

Ligand	Complex	*ee* (%) (product configuration)	Location of substituents in octants	Chirality in configurational models	
				Pr/*Mr*	Pr^{oct}/Mr^{oct}
 **18**		> 99 (*S*)	FL(+), FR(+), RR(+), RL(+)	*Mr*	Pr^{oct}
 **19**		89–91 (*S*)	RL(+), RR(+)	*Pr*	Pr^{oct}
 **20**		64 (*R*)	RL(−), RR(−)	*Mr*	Mr^{oct}
 **21**		48 (*R*)	FL(−), FR(−), RL(−), RR(−)	*Pr*	Mr^{oct}

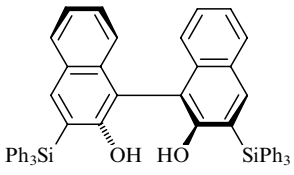
Note. Hereinafter, the following designations are used: Mr^{oct} (minus region octants); FL(−), frontal left (−); FR(−), frontal right (−); RL(−), rear left (−); RR(−), rear right (−) octants; Pr^{oct} (plus region octants), FL(+), frontal left (+); FR(+), frontal right (+); RL(+), rear left (+); RR(+), rear right (+) octants.

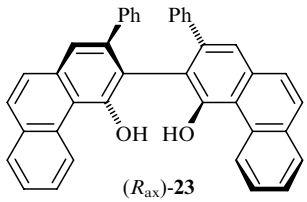
complexes with ligands **18** and **21** are located beyond quadrants that contain the chelate rings and that are limited by a plane passing through the metal atom perpendicular to the symmetry axis C_2. In the case of complexes with ligands **19** and **20**, the alkyl groups remain within the quadrants. In the framework of the *Pr*/*Mr* model, the complexes Pd–**18** and Pd–**20**, Pd–**19** and Pd–**21** are identical pairwise. Nevertheless, the configurations of the corresponding reaction products are different. It may thus be concluded that the escape of the substituent from the limits of the above-mentioned space changes the chirality sign. However, in this case the octant projection with the opposite signs of the frontal and rear octants¶ (Fig. 3) becomes applicable and the configurational *Mr*/*Pr* model is considered as a particular case of the configurational model based on the octant projection (the Mr^{oct}/Pr^{oct} model) for those complexes with ligands which do not escape the space of the rear octants.

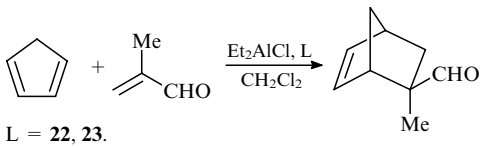
As can be seen from Table 2, the Mr^{oct}/Pr^{oct} model is more adequate to the experimentally determined enantioselectivity of this reaction.

Cycloaddition of cyclopentadiene to methacrolein catalysed by the *in situ* formed complexes Al–**22** and Al–**23** is yet another example of the difference between the models *Mr*/*Pr* and Mr^{oct}/Pr^{oct}.[80]

¶ By analogy with the octant projection used for the description of the chiral environment of the carbonyl chromophore in cyclohexanone based on data from circular dichroism.[78, 79]


(R_{ax})-**22**


(R_{ax})-**23**



L = **22**, **23**.

Complex	The sign of optical rotation of the cycloaddition product	*ee* (%)	Chirality in configurational models	Location of substituents in octants
(R_{ax})-**22**	−	17	*Pr*, Pr^{oct}	RL(+), RR(+)
(R_{ax})-**23**	+	97	*Mr*, Mr^{oct}	FL(−), FR(−)

The silicon atoms in the octant projection of the molecular model of the Al–**22** complex fall into the rear positive octants close to the plane separating the frontal and rear octants; hence, the low enantiomeric excess of the reaction product is explicable. The terminal fragments of the phenanthrene units of the ligand in

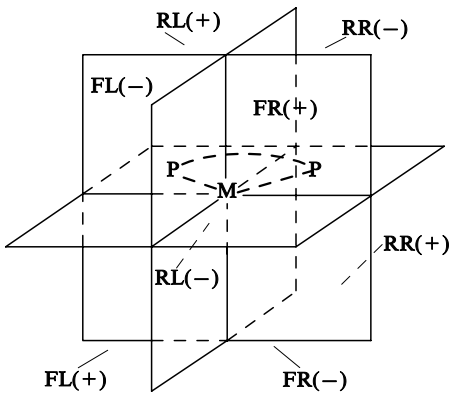
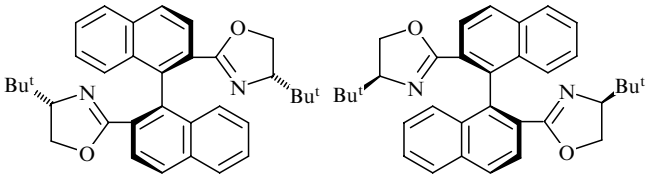


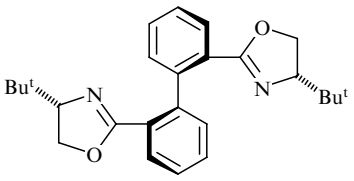
Figure 3. The octant projection of the Pd complexes **18**–**21**. The designations of the types and signs of the octants as in Legend to Table 2.

the projection of the complex Al–**23** lie in the frontal negative octants, which suggests a change in the chirality sign in comparison with the previous case. This observation is consistent with the experimental data[80] and suggests that the results obtained are better rationalised in terms of the Pr^{oct}/Mr^{oct} model than in terms of the Pr/Mr model.

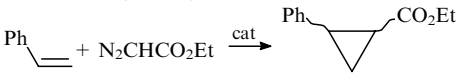
Cyclopropanation of styrene with ethyl diazoacetate in the presence of complexes CuOTf–**24** (see Ref. 81) and CuOTf–**25** (Ref. 82) is yet another illustrative example of the applicability of the octant model to the estimation of enantioselectivity.



(S_{ax},*S*,*S*)-**24** (R_{ax},*S*,*S*)-**24**



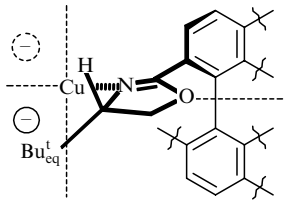
(S_{ax},*S*,*S*)-**25**



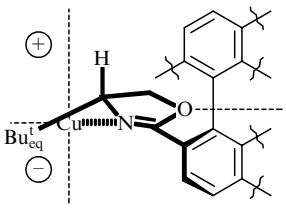
Catalyst	Isomer of ethyl 2-phenylcyclopropanecarboxylate	*ee* (%) (see †)
(S_{ax},*S*,*S*)-**24**	*trans*-(1*R*,2*R*)	87
	cis-(1*R*,2*S*)	86
(R_{ax},*S*,*S*)-**24**	*trans*-(1*S*,2*S*)	3
	cis-(1*S*,2*R*)	3
(S_{ax},*S*,*S*)-**25**	*trans*-(1*R*,2*R*)	71
	cis-(1*R*,2*S*)	84

† Chromatographic analysis of the cyclopropanation products on columns with chiral phases gives the ratio of the enantiomeric pairs *trans*-(1*S*,2*S*)/*trans*-(1*R*,2*R*) and *cis*-(1*S*,2*R*)/*cis*-(1*R*,2*S*). Therefore, the enantioselectivity of the reaction is usually expressed by *ee* values and the total ratio of the *trans*/*cis* products. If the reaction is carried out with chiral esters, the value of the diastereomeric excess [*de* (%)] is sometimes used.

The lateral projections of the first two complexes are shown below. In the projection of the Cu–(S_{ax},*S*,*S*)-**24** complex, the Bu^t_{eq} groups lie in the frontal negative octants (for simplicity's sake, the second dihydrooxazole ring in each complex is omitted). In the projection of the second complex, these groups are localised in the vicinity of the plane separating the frontal octants with the opposite signs. Presumably, such a border location is the reason for the extremely low (3%) enantioselectivity of the reaction catalysed by this complex.

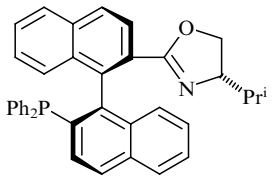


Cu-(S_{ax},*S*,*S*)-**24**

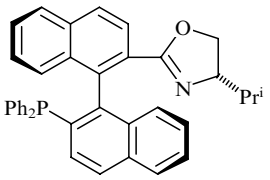


Cu-(R_{ax},*S*,*S*)-**24**

A comparison of the contributions of different types of chirality to the enantioselectivity gives rather controversial results. On the one hand, the dominant role of the axial chirality in the dihydrooxazole ring (in comparison with the central chirality) in the cyclopropanation reaction [Cu–(S_{ax},*S*,*S*)-**24** and Cu–(R_{ax},*S*,*S*)-**24**] leaves no doubt (see Ref. 81). On the other hand, the contribution of the axial chirality caused by the difference between the dinaphthyl and diphenyl systems in analogous complexes Cu–(S_{ax},*S*,*S*)-**24** (see Ref. 81) and Cu–(S_{ax},*S*,*S*)-**25** (see Ref. 82) in the same reaction is very small. As regards the central chirality of the carbon and phosphorus atoms in the complexes[69] Rh–(*S*,*S*,*S*,*S*,*S*p)-**17** and Rh–(*S*,*S*,*S*,*S*,*R*p)-**17** employed for hydrogenation (see Table 1), the data available do not allow an unambiguous conclusion. The dominant role of the axial chirality in comparison with the central chirality in the dihydroxazole fragment in the allylic alkylation of 1,3-diphenylprop-2-enyl acetate can be judged from the example of the palladium complexes with ligands (S_{ax},*S*)-**26** [(*S*), 28%] and (R_{ax},*S*)-**26** [(*R*), 86%].[83, 84]



(S_{ax},*S*)-**26**



(R_{ax},*S*)-**26**

However, even a qualitative estimation of the contribution of one or another type of chirality is not always possible.[8] Generally speaking, estimation of contributions of different types of chirality of catalytic complexes to enantioselectivity can be regarded as a formal approach to the problem. Enantioselectivity is provided by spatial fixation of bulky groups of the ligand that being nearest to the donor atoms form the chiral environment of the metal atom. In other words, the ligand molecule within a catalytic complex plays the role of a template.

The octant projections and the 'Pr^{oct} (Mr^{oct})–product configuration' relationship cannot be regarded as the quantitative reflection of the stereochemistry of these complexes. These projections simply show the probable distribution of the groups that determine the chirality of the metal environment. These results were obtained from the analysis of molecular models, *viz*., Dreiding stereomodels ('Büchi Laboratoriums-Technik AG') or the published X-ray diffraction data and calculations.

The description of the real stereochemistry of a complex suitable for predicting both the configuration of the product and *ee* is possible only if exact spatial coordinates of the environment of the bulky groups that form the chiral environment of the metal atom under the reaction conditions are known. Unfortunately, X-ray diffraction data, *e.g*., on transition metal chiral chelate

complexes,[61] can hardly be used as a reliable basis in the construction of quantitative models of the type 'structural elements of complex – *ee* and product configuration'. Equalisation of molecular parameters of complexes in 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[85] 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 the dependence of *ee* of the *endo*-adduct on the torsion angle of the biaryl 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 this case, of the biaryl fragment).[86] Correspondingly, a linear dependence exists between CCM and the dihedral angle. This testifies to the non-linear dependence between CCM and the experimentally determined *ee* value of the reaction product.[86] Most probably, the introduction of the parameter CCM[87] opens up a new way of predicting the magnitude and sign of enantioselectivity on the basis of calculations.

The majority of quantitative theoretical approaches dealing with asymmetric homogeneous catalytic reactions catalysed by metal complexes are based on computations that employ different programs and methods for different reactions and catalysts. The correspondence of the calculated parameters to the experimental results is considered as evidence in favour of a suggested mechanism. Recently, calculations have been carried out for the hydrogenation of enamides in the presence of the Rh–**2** complex;[27] for hydrogen-transfer hydrogenation of ketones catalysed by Rh–diamine,[88,89] Ru–*N*-tosylethylenediamine[90] or Ru–amino alcohol complexes,[90–92] for cyclopropanation of styrene on the complex Cu–*N*,*N*′-dimethylmalonaldiimine,[93] *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 sign of asymmetric induction and its interpretation. Many additional examples in which these models were compared can be mentioned. However, this is more appropriate in the subsequent analysis of the most extensively studied reactions catalysed by metal complexes (see Sections III–VII).

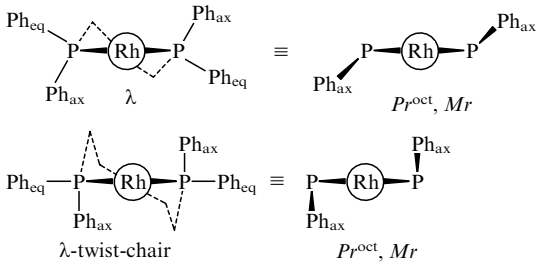
The octant projection localisation of the chiral C_2-symmetric metallacycle containing two identical donor atoms is shown in Fig. 3. The following conditions should be met when octant projections are used. In defining the sign of the octant determining the chirality, preference is given to the substituent nearest to the donor atom. Other conditions being the same, the preference is given to a bulkier substituent ($Bu^t > Pr^i > Pr^n > Et > Me$; $Bu^tCH_2 > Ph > Bn$, *etc*.). For different substituents at the same atom of the metallacycle of the complex not affecting the sign of the asymmetric induction, the complex with a substituent, which ensures the maximum value of *ee* of the reaction product, is allowed for. If the changes in the reaction conditions (*e.g*., solvent, temperature, additional reagent, *etc*.) do not cause any reversal of the product configuration, they are excluded from consideration.

Additional conditions should be met in order to unify the approach to the description of this model. In the octant projection (a view from the metal side) of an asymmetric metallacycle containing two identical donor atoms, the atom with a substituent determining the octant sign (which is closer to the donor atom or is bulkier) occupies a right-sided position; in the presence of two different donor atoms, the inferior (as regards its atomic number) atom takes a right-sided position; preference is given to the substituent or the environment of the left (senior) donor atom.

It is necessary that the last three requirements are met for the standardisation of the subjects that are analysed. The requirement for the unification is extended to the choice of relevant data for a concrete substrate in reactions carried out under maximally similar conditions.

‡ By analogy with the terms 'chromophore' and 'pharmacophore'.

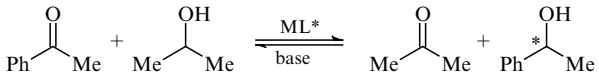
Determination of octant projections of various complexes is based on the use of molecular models or X-ray diffraction data. For example, the octant projections of bis(diphenylphosphine) complexes were obtained on the basis of data on the λ- and δ- as well as λ- and δ-twist-chair conformations of five- and seven-membered rhodium chelate complexes.[10]



This projection shows only axial phenyl substituents. They fall completely into the corresponding octants, whereas the equatorial substituents lie at the border between two opposite octants. Therefore, the chirality of a complex is determined from the position of the axial substituents in the octants.

III. Hydrogen-transfer hydrogenation of acetophenone catalysed by metal complexes

Hydrogenation of aromatic ketones is one of the simplest asymmetric reactions catalysed by metal complexes with different chiral ligands.[16,94,95]



A comparison of the '*Pr*(*Mr*)–product configuration' and '$Pr^{oct}(Mr^{oct})$–product configuration' relationships for the hydrogen-transfer hydrogenation of acetophenone in the presence of rhodium and iridium complexes is presented in Table 3. Those complexes with bidentate ligands are considered where the spatial configurations of the bulky groups adjacent to the metal atom that determine its chiral environment are established on the basis of molecular models or using X-ray diffraction. As can be seen, the relationships Pr^{oct}–(*S*), Mr^{oct}–(*R*) and *Pr*–(*R*), *Mr*–(*S*) are observed in 60% and 53% of cases, respectively. An analysis of other complexes including ruthenium complexes (Table 4) revealed that the relationships Pr^{oct}–(*R*), Mr^{oct}–(*S*) and *Pr*–(*R*), *Mr*–(*S*) are observed in 70% and 80% of cases.

Special attention in Tables 3 and 4 should be paid to the relatively low enantioselectivity of reactions in the presence of complexes with chiral C_2-symmetric ligands. The *ee* values of the reaction product increase significantly on going to complexes with asymmetric ligands. At the first glance, this conclusion is contradictory to the high enantioselectivity of acetophenone hydrogenation catalysed by complexes containing chiral C_2-symmetric tri- and tetradentate ligands **56**–**59**[119–123] (Table 5).§ However, as can be seen from Table 5, the *ee* values and the configurations of the products formed in the presence of complexes with these ligands and of complexes with ligands which represent 'monomeric' analogues of these complexes, are virtually identical, which probably suggests that it is on these asymmetric 'monomeric' fragments that the reaction occurs. Indeed, excessive shielding of the metal atom, which fulfils the catalytic function, with bulky groups of tri- and tetradentate ligands prevents substrate coordination. Besides, the results of molecular model studies suggest that considerable stress is required for the ligand **59** to be coordinated

§ In the presence of some complexes with chiral C_2-symmetric tridentate ligands, this reaction proceeds with low enantioselectivity ($ee_{max} \leqslant 45\%-48\%$).[124,125]

Table 3. Comparison of the configurational models *Pr*/*Mr* and Pr^{oct}/Mr^{oct} in the hydrogen-transfer hydrogenation of acetophenone catalysed by rhodium and iridium complexes.

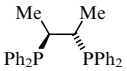
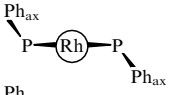
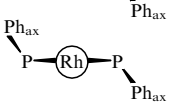
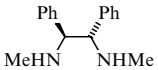
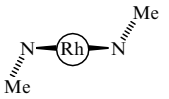
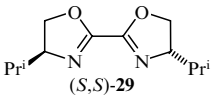
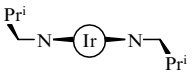
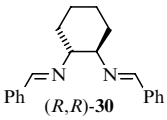
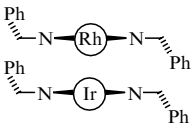
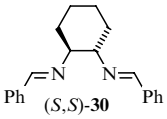
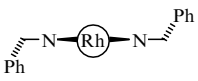
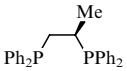
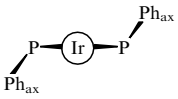
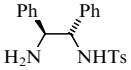
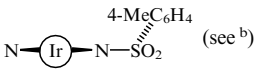
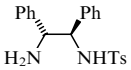
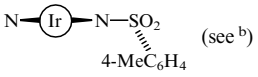
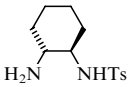
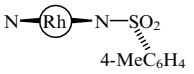
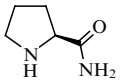
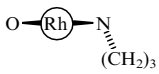
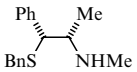
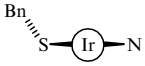
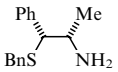
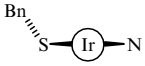
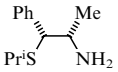
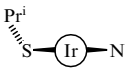
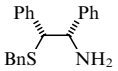
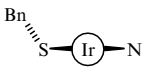
Ligand	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (configuration of 1-phenylethan-1-ol)	Ref.
			Pr^{oct}/Mr^{oct}	*Pr*/*Mr*		
Complexes with chiral C_2-symmetric ligands						
 (*S*,*S*)-**27**		FR(−), FL(−)	Mr^{oct}	*Pr*	< 1	96
(*R*,*R*)-**5**		FR(−), FL(−)	Mr^{oct}	*Pr*	< 1	96
 (*S*,*S*)-**28**	 (see [a])	RR(−), RL(−)	Mr^{oct}	*Mr*	67 (*R*)	96
 (*S*,*S*)-**29**		FR(−), FL(−)	Mr^{oct}	*Pr*	58 (*R*)	98
 (*R*,*R*)-**30**		RR(+), RL(+) the same	Pr^{oct} Pr^{oct}	*Pr* *Pr*	48 (*S*) 41 (*S*)	99 99
 (*S*,*S*)-**30**		RR(−), RL(−)	Mr^{oct}	*Mr*	45 (*R*)	99
Complexes with asymmetric ligands						
 (*R*)-**31**		FR(+), FL(+)	Pr^{oct}	*Mr*	58 (*S*)	100
 (*S*,*S*)-**32**	 (see [b])	RR(+)	Mr^{oct}	*Mr*	90 (*S*)	102
 (*R*,*R*)-**32**	 (see [b])	RR(−)	Pr^{oct}	*Pr*	96 (*R*)	103
 (*R*,*R*)-**33**		RR(−)	Pr^{oct}	*Pr*	97 (*R*)	103
 (*S*)-**34**		RR(+)	Pr^{oct}	*Pr*	59 (*R*)	104
 (*R*,*S*)-**35**		RL(+)	Pr^{oct}	*Pr*	82 (*S*)	105
 (*R*,*S*)-**36**		RL(+)	Pr^{oct}	*Pr*	65 (*S*)	105

Table 3 (continued).

Ligand	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (configuration of 1-phenylethan-1-ol)	Ref.
			Pr^{oct}/Mr^{oct}	Pr/Mr		
Complexes with asymmetric ligands						
 (*R*,*S*)-**37**		RL(+)	Pr^{oct}	*Pr*	73 (*S*)	105
 (*R*,*S*)-**38**		RL(+)	Pr^{oct}	*Pr*	80 (*R*)	105

Note. Here and in the subsequent Tables, a schematic projection of the metallacycle onto the plane perpendicular to the XMY plane passing through the metal atom is given (X and Y are the donor atoms of the ligand; M is metal).
[a] Calculated by the DFT method (see Refs 89 and 97). [b] According to X-ray diffraction data[101] for the complex Rh – [(*S*,*S*)-**32**].

Table 4. Comparison of the configurational models Pr/Mr and Pr^{oct}/Mr^{oct} in the hydrogen-transfer hydrogenation of acetophenone catalysed by ruthenium and zirconium complexes.

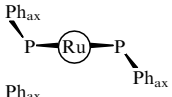
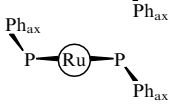
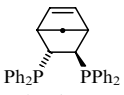
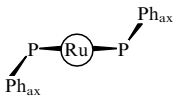
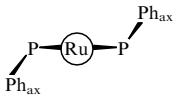
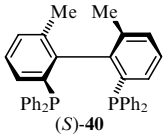
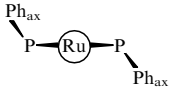
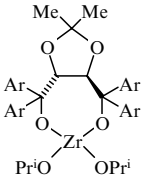
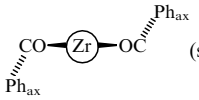
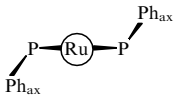
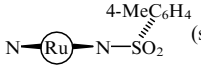
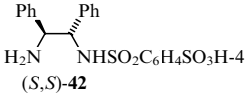
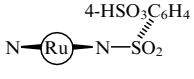
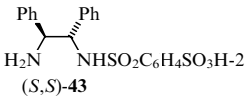
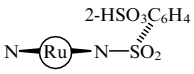
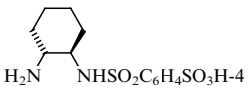
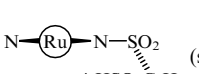
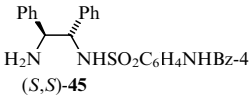
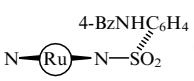
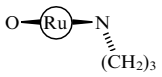
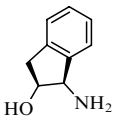
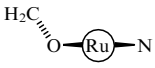
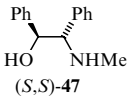
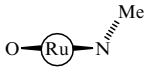
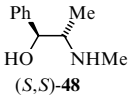
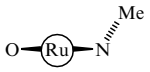
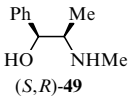
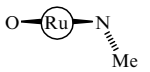
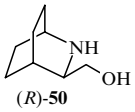
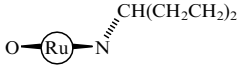
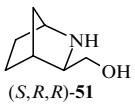
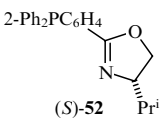
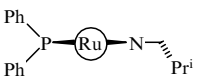
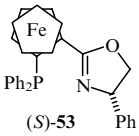
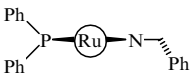
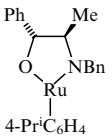
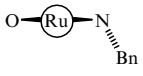
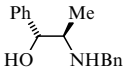
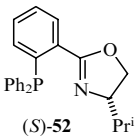
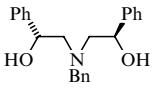
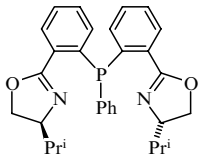
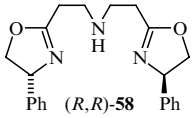
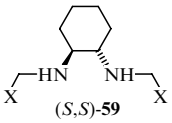
Ligand	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (configuration of 1-phenylethan-1-ol)	Ref.
			Pr^{oct}/Mr^{oct}	Pr/Mr		
Complexes with chiral C_2-symmetric ligands						
(*S*,*S*)-**27**		FR(−), FL(−)	Mr^{oct}	*Pr*	1 (*S*), 30(*R*)	106
(*R*,*R*)-**5**		FR(−), FL(−)	Mr^{oct}	*Pr*	2 (*R*), 8 (*S*)	106
 (*R*,*R*)-**39**		FR(+), FL(+)	Pr^{oct}	*Mr*	28 (*R*)	106
(*R*)-**3**		FR(+), FL(+)	Pr^{oct}	*Mr*	30 (*S*)	106
 (*S*)-**40**		FR(−), FL(−)	Mr^{oct}	*Pr*	15 (*R*)	106
 Zr–(*R*,*R*)-**41** (Ar = H, C_6H_4OMe-4)	 (see [a])	RR(−), RR(−)	Mr^{oct}	*Mr*	40 (*R*)	107
Complexes with asymmetric ligands						
(*R*)-**31**		FR(+), FL(+)	Pr^{oct}	*Mr*	52 (*S*)	106
(*S*,*S*)-**32**	 (see [b])	RR(+)	Mr^{oct}	*Mr*	90 – 98 (*S*)	102, 108 – 110
 (*S*,*S*)-**42**		RR(+)	Mr^{oct}	*Mr*	94 (*S*)	111

Table 4 (continued).

Ligand	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (configuration of 1-phenylethan-1-ol)	Ref.
			Pr^{oct}/Mr^{oct}	Pr/Mr		
Complexes with asymmetric ligands						
 (*S*,*S*)-**43**		RR(+)	Mr^{oct}	*Mr*	91 (*S*)	111
 (*R*,*R*)-**44**	 (see [b])	RR(−)	Pr^{oct}	*Pr*	88 (*R*)	111
 (*S*,*S*)-**45**	 (see [b])	RR(+)	Mr^{oct}	*Mr*	96.5 (*S*)	112
(*S*)-**34**		RR(+)	Pr^{oct}	*Pr*	79 (*R*)	104
 (*S*,*R*)-**46**		RL(+)	Pr^{oct}	*Pr*	91 (*S*)	113
 (*S*,*S*)-**47**		RR(−)	Mr^{oct}	*Mr*	92 (*S*)	114
 (*S*,*S*)-**48**		RR(−)	Mr^{oct}	*Mr*	89 (*S*)	114
 (*S*,*R*)-**49**		RR(+)	Pr^{oct}	*Pr*	91 (*S*)	114
 (*R*)-**50**		RR(−)	Mr^{oct}	*Mr*	95 (*S*)	115
 (*S*,*R*,*R*)-**51**		RR(−)	Mr^{oct}	*Mr*	94 (*S*)	115
 (*S*)-**52**		FR(−)	Pr^{oct}	*Pr*	86 (*R*)	116
 (*S*)-**53**		FR(−)	Pr^{oct}	*Pr*	94 (*R*)	117
 (*R*,*R*)-**54**		RR(+)	Pr^{oct}	*Pr*	95 (*R*)	92, 118

[a] X-Ray diffraction data of the complex Ti–[(*R*,*R*)-**41**]$_2$ (see Ref. 107). [b] Data from X-ray diffraction analysis.[101]

Table 5. Asymmetric hydrogen-transfer hydrogenation of acetophenone catalysed by complexes with chiral C_1-symmetric bidentate (monomeric) ligands and chiral C_2-symmetric tri- and tetradentate (dimeric) ligands.

Ligand	Complex	*ee* (%)	Product configuration	Ref.
Monomeric ligands				
 (*R*,*R*)-**55**	Ru–(*R*,*R*)-**55**	95	*R*	92, 118
 (*S*)-**52**	Ru–(*S*)-**52**	86	*R*	116
(*R*)-**52**	Ru–(*R*)-**52**	86	*S*	116
Dimeric ligands				
 (*R*,*R*)-**56**	Sm–[(*R*,*R*)-**56**]$_2$	96	*R*	119
 (*S*,*S*)-**57**	Ru–[(*S*,*S*)-**57**]$_2$	79	*R*	120
 (*R*,*R*)-**58**	Ru–[(*R*,*R*)-**58**]$_2$	97	*S*	121
 (*S*,*S*)-**59** (X = $C_6H_4PPh_2$-2)	Ru–(*S*,*S*)-**59**	97	*R*	122, 123
(*R*,*R*)-**59**	Ru–(*R*,*R*)-**59**	96	*S*	122, 123

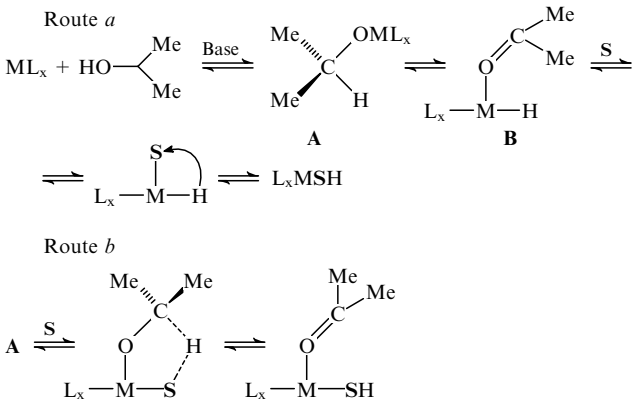
within the complex through all the four donor atoms. A similar assumption based on a larger body of experimental evidence according to which complexes with asymmetric fragments (but not complexes with chiral C_2-symmetric tri- and tetradentate ligands) are involved in the catalytic reaction will be considered in Section VII.

The position of substituents in certain complexes is sometimes difficult to establish with the use of molecular models, although asymmetric hydrogenation of acetophenone on these complexes proceeds with sufficiently high enantioselectivity.[126–134]

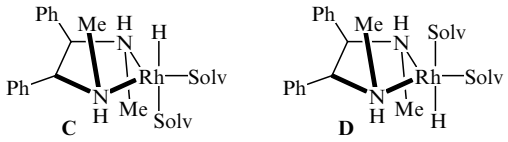
Two mechanisms of the hydrogen-transfer hydrogenation of ketones are currently being considered,[6,95,105] *viz*., route *a* (hydride route) and route *b* (direct hydrogen transfer) (Scheme 1).

Route *a* seems to be more substantiated,[97] since the hydride intermediate **B**, which adds the substrate, was detected experimentally.[135] According to DFT calculations,[89] the structure of the metallacycle containing stereogenic nitrogen atoms (the symmetry axis C_2) is the most stable in the case of the chiral C_2-symmetric ligand. By illustration, in the case of (*R*,*R*)-*N*,*N*′-dimethyl-1,2-diphenylethylenediamine (*R*,*R*)-**28** and the catalytic system

Scheme 1

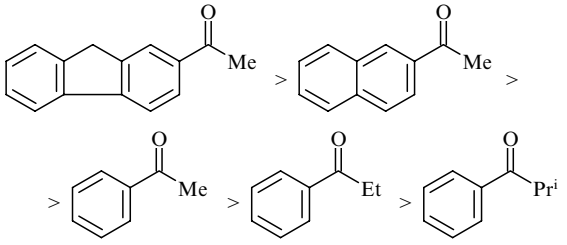


[RhCl(COD)]$_2$–(*R*,*R*)-**28** (COD is cycloocta-1,5-diene) the structures **C** and **D** can be formed.



If structures **C** and **D** are at equilibrium and the asymmetric induction in the substrate coordination step proceeds at a slower rate, the substrate can recognise the chiral environment of the metal atom as a C_2-symmetric environment.

We have obtained some experimental evidence[6,99] in favour of the asymmetric induction of hydrogen-transfer hydrogenation of aromatic ketones during their coordination on rhodium and iridium complexes [Rh–(*R*,*R*)-**30**, Rh–(*S*,*S*)-**30**, Ir–(*R*,*R*)-**30**, *etc*.].

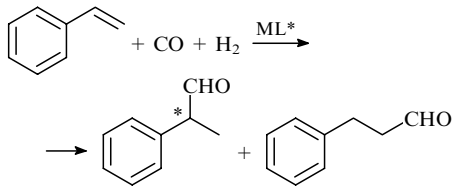


The order of changes in the *ee* values of the reaction products in the ketone series suggests that enantiodiscrimination by catalytic complexes correlates with the molecular sizes of substituents in prochiral aromatic ketones. The direct proportionality between these parameters is in favour of the asymmetric induction in the direct interaction of the catalytic complex with the substrate (ketone), *i.e*., during the coordination of the substrate.

Thus, the enantioselectivity of the hydrogen-transfer hydrogenation of acetophenone on rhodium, iridium and ruthenium complexes depends on the symmetry of a catalytic complex. Complexes with chiral C_1-symmetric (asymmetric) ligands manifest higher enantioselectivity than complexes with chiral C_2-symmetric ligands. Probably, the asymmetric induction takes place in the coordination of the carbonyl group of the ketone by the C_2-symmetric chiral hydride complex (in the case of a C_2-symmetric starting complex). In complexes with asymmetric ligands, the asymmetric induction is controlled by the asymmetric hydride complex. In some other reactions,[6] asymmetric intermediates also ensure high enantioselectivity.

IV. Catalytic hydroformylation of styrene in the presence of metal complexes

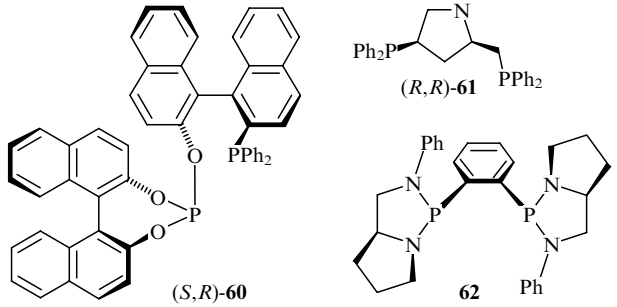
Hydroformylation of alkenes on chiral metal complexes is one of the most prominent industrially important reactions in asymmetric catalysis.[3, 47, 136–138] Several types of such reactions exist that differ in the positions of the double bonds in alkenes and the pathway of formation of chiral carbon atoms in the reaction products. Hydroformylation of styrene is especially well studied.



Platinum and rhodium complexes with phosphine and phosphinite ligands as catalysts provide the highest enantioselectivity.

Correlation of the *ee* values and the configurations of the products with the arrangement of the substituents which determine the chiralities of the corresponding complexes in the octants (the octant projection) or quadrants (the quadrant projection) suggests that the regularities $Mr^{oct}-(S)$, $Pr^{oct}-(R)$ and $Pr-(S)$, $Mr-(R)$ are fulfilled similarly in both cases for both platinum [40, 41, 45, 139–145] and rhodium complexes.[41, 46, 146, 147]

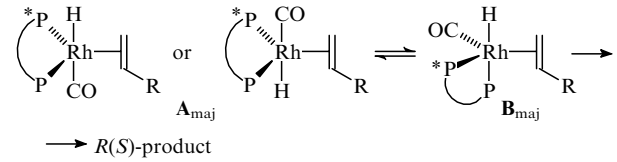
A comparison of enantioselectivities in the hydroformylation of styrene catalysed by rhodium complexes with chiral C_2-symmetric ligands and chiral C_1-symmetric (asymmetric) ligands revealed that as in the hydrogen-transfer hydrogenation, complexes containing C_2-symmetric ligands [148–154] are noticeably less enantioselective than complexes with asymmetric ligands [115, 155–162] of the type (*S*,*R*)-**60** (*ee* = 94%) or (*R*,*R*)-**61** (*ee* > 96%).[161, 162]

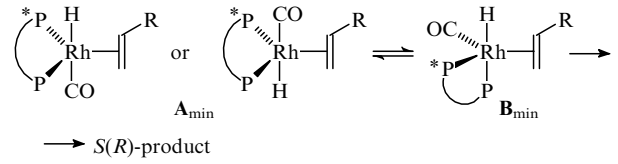


The lack of enantioselectivity in the reaction catalysed by a rhodium complex with the chiral C_2-symmetric ligand **62** (*ee* = 0) is especially surprising.[153] This ligand manifests a virtually ideal C_2-symmetry due to the conformational rigidity of the bicyclic systems at the donor phosphorus atoms.

For complexes with sulfur-containing bidentate ligands [163, 164] or ligands based on donor sulfur and phosphorus atoms,[165] or phosphorus and nitrogen atoms [166, 167] or bis(dialkylphosphine) complexes,[168] the enantioselectivity of styrene hydroformylation is rather low.

The known mechanisms of asymmetric hydroformylation of alkenes on rhodium diphosphine complexes [136, 154] suggest competition between two pairs of diastereomeric intermediates **A** and **B**,[169] which have the shape of trigonal bipyramids.



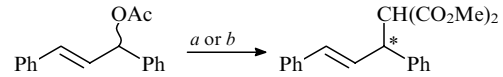


These intermediates determining the direction of the asymmetric induction represent constituents of stereoisomeric minor and major cycles. If the starting compounds represent chiral C_2-symmetric complexes and the equilibrium is established rather quickly, the chiral fragments of the intermediates $\mathbf{A}_{maj}$ and $\mathbf{A}_{min}$ are considered to be C_2-symmetric with respect to the coordination substrate.

Thus, the enantioselectivities of alkene hydroformylation on rhodium diphosphine complexes and hydrogen-transfer hydrogenation of ketones on rhodium, iridium and ruthenium complexes are determined by the symmetry of the catalytic complex. Chiral C_1-symmetric (asymmetric) complexes provide higher enantioselectivity in comparison with chiral C_2-symmetric complexes.[170] Apparently, the asymmetric induction occurs in the coordination of alkenes on chiral C_2-symmetric intermediates, the starting complex being chiral and C_2 -symmetric. In complexes containing asymmetric ligands, the asymmetric induction is effected by the asymmetric intermediate. Similar to other reactions,[6] asymmetric intermediates provide higher enantioselectivity.

V. Allylic alkylation catalysed by palladium complexes

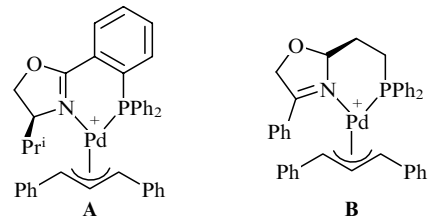
Among other asymmetric allylic alkylation reactions catalysed by palladium complexes,[171–176] the reaction with 1,3-diphenylprop-2-enyl acetate is especially well-studied.



(*a*) $[Ph(\eta^3\text{-}C_3H_5)Cl]_2$/L*, $NaCH(CO_2Me)_2$; (*b*) $[Pd(\eta^3\text{-}C_3H_5Cl]_2$/L*, $CH_2(CO_2Me)_2$, *N,O*-bis(trimethylsilyl)acetamide, AcOK.

Although the reaction product probably does not represent a valuable synthon, this reaction is very popular for a number of reasons. First, large dimensions of both the substrate and the nucleophile molecules ensure a high level of discrimination of the reaction in the presence of a catalytic complex and, as a consequence, its high enantioselectivity. Second, the nature of palladium as a complex-forming metal allows the use of diverse ligands that do not reduce the catalytic properties of the complex in this reaction.

In the allylic alkylation of 1,3-diphenylprop-2-enyl acetate with diethyl malonate in the presence of palladium complexes with several ligands, a series of intermediates with a coordinated allylic substrate was isolated and their structures were established by X-ray diffraction analysis.[177–179] The bulky, spatially extended molecule of the coordinated substrate in these intermediates shifts the ligand fragments to the rear octants (the octant projection). However, such a shift should be considered as a trend rather than a rule. Thus the phenyl substituent in the oxazoline ligand fragment of the complex **B** falls into the frontal octant.[179]

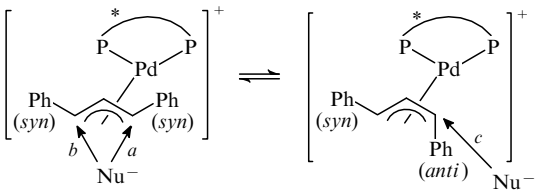


As the asymmetric induction takes place in the attack of the nucleophile on the intermediate containing a coordinated allylic group (see below), the distribution of substituents in the octants should be estimated for these intermediates. The projections and the distributions of substituents in palladium chiral C_2-symmetric diphosphine and diphosphinite complexes in the octants and quadrants as well as *ee* values and the configuration of the allylic alkylation product of 1,3-diphenylprop-2-enyl acetate by diethyl malonate in the presence of these complexes are listed in Table 6. As can be seen, in 70% of cases the formation of allylic alkylation products conforms to the rule: Pr^{oct}–(*S*), Mr^{oct}–(*R*). The configurational model *Pr*/*Mr*–(*S*)/(*R*) is fulfilled with a ~50% probability, *i.e.*, the rule based on quadrant projections is inapplicable to this case.

The enantioselectivity of the reaction catalysed by palladium diphosphinite complexes depends, to a large measure, on the nature of the substituents at the phosphorus atoms of the ligand (see data from the complexes Pd–**66**, Table 6).

The enantioselectivity of this reaction can be explained by steric and electronic factors, *e.g.*, the effects of substituents on the relative activities of two terminal allylic positions attacked by a nucleophile (Scheme 2, routes *a*, *b*) or *syn*,*syn*/*syn*,*anti*-isomerism (Scheme 2, route *c*).[71]

Scheme 2



All three routes are associated with changes in the product configuration. The contribution of steric factors due to the energy gain in the case of the equatorial position of bulky substituents in the chelate ring (*cf.* Ref. 77) is presumably [71] compensated for by the effects of electronic factors. It is rather difficult to detect electronic effects in the background of the steric effects in reactions carried out in the presence of complexes with ligands that form seven-membered chelate rings [71] because of the high conformational labilities of these complexes.

Table 6. Allylic alkylation of 1,3-diphenylprop-2-enyl acetate with diethyl malonate in the presence of palladium chiral C_2-symmetric diphosphine and diphosphinite complexes.

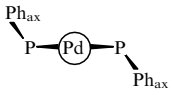
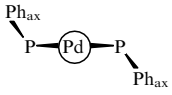
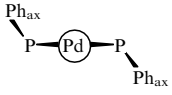
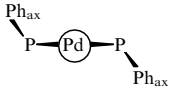
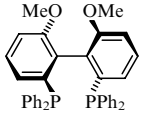
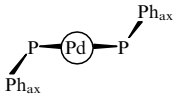
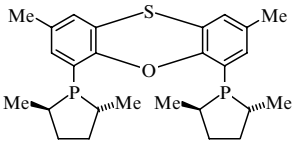
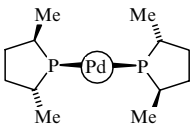
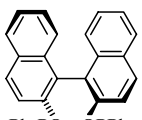
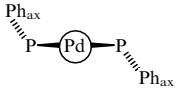
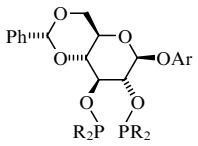
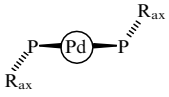
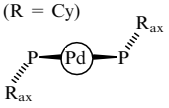
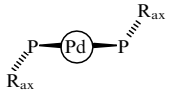
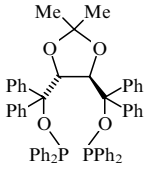
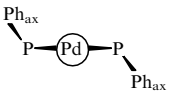
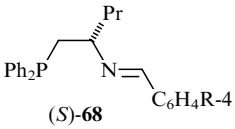
Ligand	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (product configuration)	Ref.
			Pr^{oct}/Mr^{oct}	*Pr*/*Mr*		
(*S*,*S*)-**39**		FR(−), FL(−)	Mr^{oct}	*Pr*	81 (*R*)	180
(*S*,*S*)-**27**		FR(−), FL(−)	Mr^{oct}	*Pr*	90 (*R*)	180
(*S*)-**3**		FR(−), FL(−)	Mr^{oct}	*Pr*	30 (*R*)	180
(*R*)-**40**		FR(−), FL(−)	Mr^{oct}	*Pr*	90 (*S*)	177
 (*S*)-**63**		FR(+), FL(+)	Pr^{oct}	*Mr*	87 (*R*)	177
 (*R*,*R*,*R*,*R*)-**64**		FL(−), FR(−)	Mr^{oct}	*Mr*	97 (*R*)	181
 (*R*)-**65**	 (see [a])	RL(+), RR(+)	Pr^{oct}	*Pr*	63–80 (*R*)	71

Table 6 (continued).

Ligand	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (product configuration)	Ref.
			Pr^{oct}/Mr^{oct}	Pr/Mr		
 (1*R*,2*S*,3*R*,4*S*,5*R*)-**66**	 (R = Cy)	RL(−), RR(−)	Mr^{oct}	*Mr*	59 (*R*)	71
	 (R = 3,5-$(CF_3)_2C_6H_3$)	RL(−), RR(−)	Mr^{oct}	*Mr*	39 (*R*)	71
	 (R = 4-$CF_3C_6H_4$)	RL(−), RR(−)	Mr^{oct}	*Mr*	55 (*R*)	71
 (*R*,*R*)-**67**	 (see [b])	FL(−), FR(−)	Mr^{oct}	*Pr*	76 (*R*)	59, 182

Note. Cy is cyclohexyl. [a] Calculation (see Ref. 182). [b] X-Ray diffraction data.[59]

The ligand **68** forms a palladium complex with a conformationally more rigid five-membered metallacycle; therefore, it represents a more convenient subject for this study.[183]

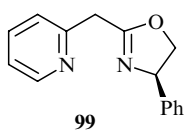


(*S*)-**68**

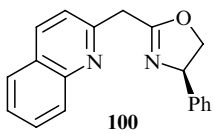
R	H	CO_2Me	CF_3	Me	OMe	NMe_2
ee, %	52 (*R*)	19 (*R*)	38 (*R*)	74 (*R*)	85 (*R*)	92 (*R*)

It has been found that electron-withdrawing groups decrease enantioselectivity, while electron-donor groups increase it. The effects of purely electronic factors on the enantioselectivity can be judged from a comparison of ligands with 4-CF_3 and 4-Me groups. Their steric effects are virtually similar, but *ee* values are significantly different. Hence, electronic factors influence *ee*, but not the product configuration.

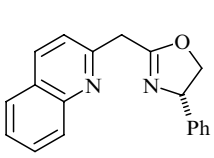
The data on the allylic alkylation of 1,3-diphenylprop-2-enyl acetate by diethyl malonate in the presence of conformationally rigid Pd complexes are summarised in Table 7. The positions of the substituents in the ligands can be determined using molecular models and based on the data for the complexes the structures of which were established by X-ray diffraction analysis or by calculations.



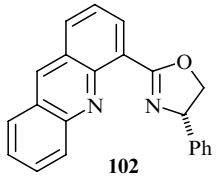
99



100



101



102

Ligand	*ee* (%)	Product configuration
(*R*)-**99**	16	*R*
(*R*)-**100**	78	*S*
(*S*)-**101**	75	*R*
(*S*)-**102**	34	*R*

The sign of enantioselectivity for the complexes with the ligands (*R*)-**100**, (*S*)-**101** and (*S*)-**102**[190] not included in Table 7 is opposite to that expected based on the corresponding data for the complexes Pd–**80** (see Table 7) and Pd–**99**. It is suggested[190] that two diastereomeric intermediates, **A** and **B** (Scheme 3), exist, which are converted into the π-complexes **C**–**F** by four different routes. Different reactivities of these intermediates also contribute to the stereochemistry of the reaction products. The intermediates **C** and **E** are preferable for complexes with ligands of the type **99**, whereas the intermediates **D** or **F** are more typical of complexes with ligands of the type **100**. This is due to the steric interactions of the left chiral centre in the complexes **C** and **E** containing an isoquinoline fragment. The transition from the complex **C** to **D** or from **E** to **F** should be accompanied by configurational changes in the reaction product, which is the case.

As can be seen from Table 7, the dependences Pr^{oct}–(*S*), Mr^{oct}–(*R*) and *Pr*–(*S*), *Mr*–(*R*) are fulfilled in 95% and 80% of cases, respectively. Besides, the model *Pr*/*Mr* is inapplicable in a few cases (see ligands **89**–**91**). Therefore, the octant model is preferable for this reaction.

Table 7. Allylic alkylation of 1,3-diphenylprop-2-enyl acetate with diethyl malonate in the presence of chiral C_2-symmetric and asymmetric palladium complexes.

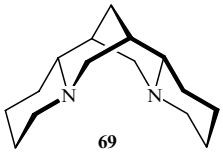
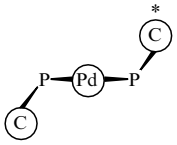
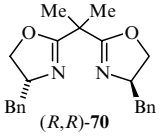
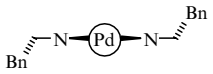
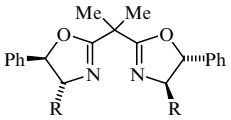
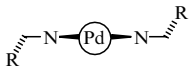
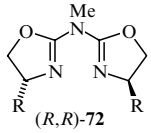
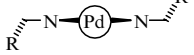
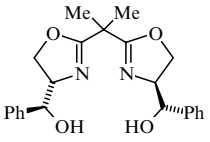
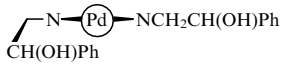
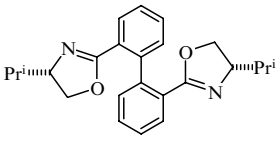
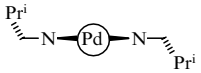
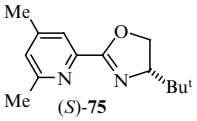
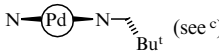
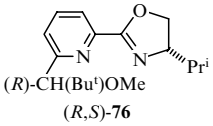
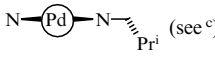
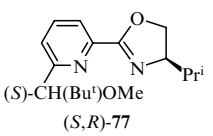
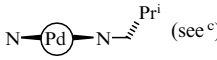
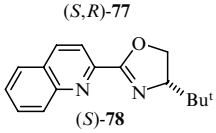
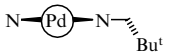
Ligand	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (product configuration)	Ref.
			Pr^{oct}/Mr^{oct}	Pr/Mr		
Complexes with chiral C_2-symmetric ligands						
 **69**		FL(+), FR(+)	Pr^{oct}	Mr	88 (*R*)	184
 (*R*,*R*)-**70**	 (see [a])	RL(−), RR(−)	Mr^{oct}	Mr	88 (*R*)	186
 (*R*,*R*,*R*,*R*)-**71** (R = $CH_2OSiMe_2Bu^t$)	 (see [a])	RL(−), RR(−)	Mr^{oct}	Mr	97 (*R*)	185
 (*R*,*R*)-**72** (R = $CH_2OSiMe_2Bu^t$)	 (see [a])	RL(−), RR(−)	Mr^{oct}	Mr	95 (*R*)	186
 (*R*,*S*,*R*,*S*)-**73**	 (see [b])	FL(+)	Pr^{oct}	Mr	92 (*S*)	187
 (*S*,*S*)-**74**		RL(+), RR(+)	Pr^{oct}	Pr	89 (*S*)	188
Complexes with asymmetric ligands						
 (*S*)-**75**	 (see [c])	RR(+)	Pr^{oct}	Pr	93 (*S*)	190
 (*R*)-CH(Bu^t)OMe (*R*,*S*)-**76**	 (see [c])	RR(+)	Pr^{oct}	Pr	99 (*S*)	191
 (*S*)-CH(Bu^t)OMe (*S*,*R*)-**77**	 (see [c])	RR(−)	Mr^{oct}	Mr	>99 (*R*)	191, 192
 (*S*)-**78**		RR(+)	Pr^{oct}	Pr	92 (*S*)	190

Table 7 (continued).

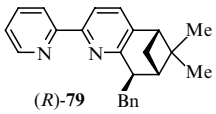
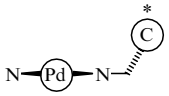
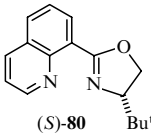
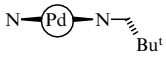
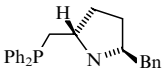
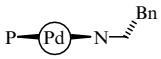
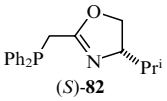
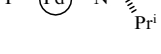
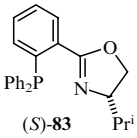
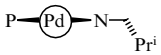
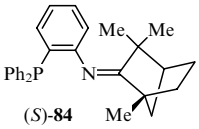
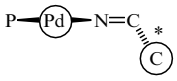
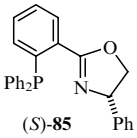
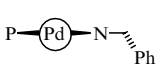
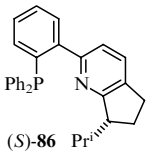
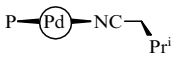
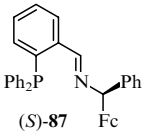
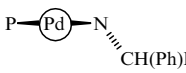
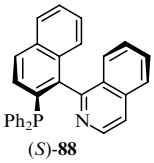
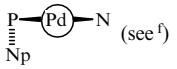
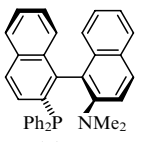
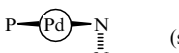
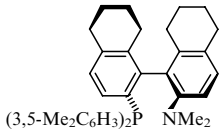
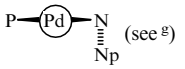
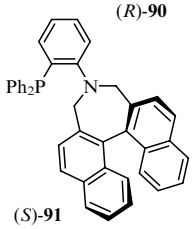
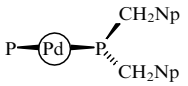
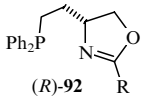
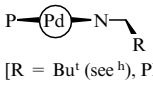
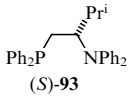
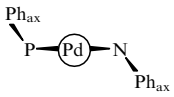
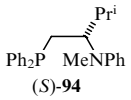
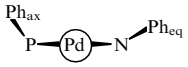
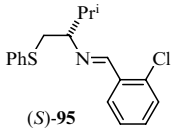
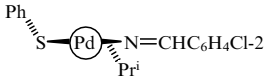
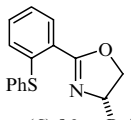
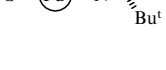
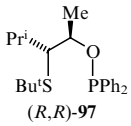
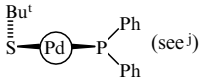
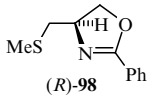
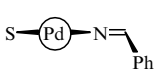
Ligand	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (product configuration)	Ref.
			Pr^{oct}/*Mr*^{oct}	*Pr*/*Mr*		
Complexes with asymmetric ligands						
 (*R*)-**79**		RR(−)	*Mr*^{oct}	*Mr*	89 (*R*)	193, 194
 (*S*)-**80**		RR(+)	*Pr*^{oct}	*Pr*	77 (*S*)	195
 (*S*)-**81**		RR(−)	*Mr*^{oct}	*Mr*	74 (*R*)	196
 (*S*)-**82**		RR(+)	*Pr*^{oct}	*Pr*	73 (*S*)	197
 (*S*)-**83**	 (see [d])	RR(+)	*Pr*^{oct}	*Pr*	98 (*S*)	197–200
 (*S*)-**84**		RR(+)	*Pr*^{oct}	*Pr*	53–90 (*S*)	198
 (*S*)-**85**	 (see [d])	RR(+)	*Pr*^{oct}	*Pr*	99 (*S*) 92 (*S*) 94–99 (*S*)	201 202 203
 (*S*)-**86**		FR(−)	*Mr*^{oct}	*Pr*	98 (*S*)	204, 205
 (*S*)-**87**	 (see [e])	RR(+)	*Pr*^{oct}	*Pr*	87 (*S*)	206
 (*S*)-**88**	 (see [f])	RL(−)	*Mr*^{oct}	*Mr*	98 (*R*)	178
 (*R*)-**89**	 (see [g])	RL(+), RR(+), FL(+), FR(+)	*Pr*^{cot}	*Mr*/*Pr*	71 (*S*) 67(*S*)	207 208

Table 7 (continued).

Ligand	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (product configuration)	Ref.
			Pr^{oct}/Mr^{oct}	Pr/Mr		
Complexes with asymmetric ligands						
 (*R*)-**90**	 (see [g])	RL(+), RR(+), FL(+), FR(+)	Pr^{oct}	Mr/Pr	84 (*S*)	208
 (*S*)-**91**		FR(+), RR(+)	Pr^{oct}	Mr/Pr	96 (*S*)	209
 (*R*)-**92**	 [R = Bu^t (see [h]), Ph]	FR(−)	Mr^{oct}	Pr	98 (*R*)	179
 (*S*)-**93**		FR(−), FL(−)	Mr^{oct}	Pr	92 (*R*)	210
 (*S*)-**94**		FL(−), FR(+)	Pr^{oct}	Mr	83 (*S*)	210
 (*S*)-**95**	 (see [i])	RL(+), RR(+)	Mr^{oct}	Pr	94 (*R*)	211
		RR(+)	Pr^{oct}	Pr	> 96 (*S*)	202
(*S*)-**96** Bu^t						
 (*R*,*R*)-**97**	 (see [j])	RL(+)	Pr^{oct}	Pr	98 (*S*)	212
 (*R*)-**98**		FR(−)	Mr^{oct}	Pr	56 (*R*)	213

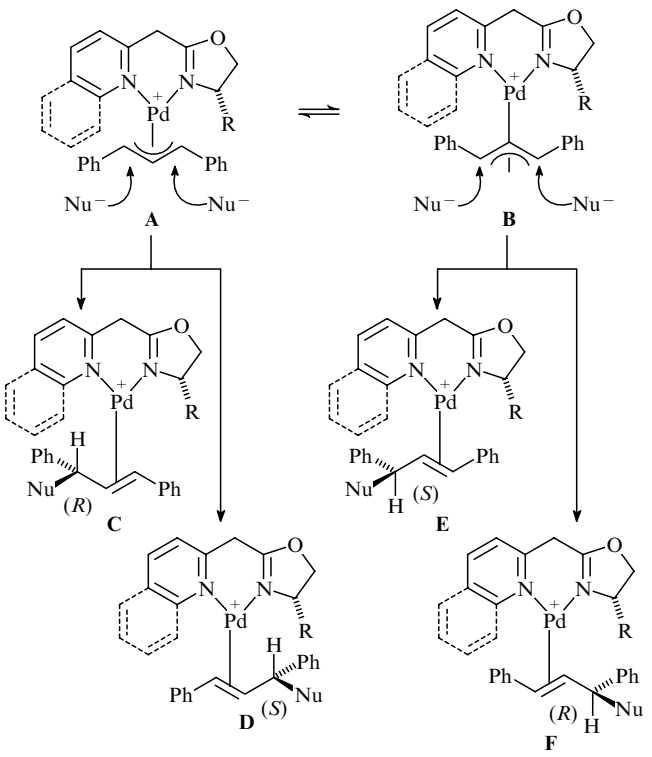
Note. Hereinafter, the molecular mass centre of a substituent or a ligand fragment is marked with an asterisk. [a] X-Ray diffraction data (see Ref. 185). [b] X-Ray diffraction data (see Ref. 187). [c] X-Ray diffraction data (see Ref. 189). [d] X-Ray diffraction data (see Refs 179 and 199). [e] Calculation (see Ref. 206). [f] X-Ray diffraction data (see Ref. 178). [g] X-Ray diffraction data (see Ref. 207). [h] X-Ray diffraction data (see Ref. 179). [i] X-Ray diffraction data (see Ref. 211). [j] X-Ray diffraction data (see Ref. 212).

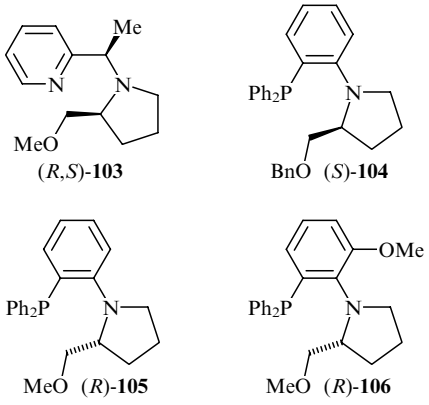
The enantioselectivities of the majority of the complexes with ligands listed in Table 7 are close to 90% or higher. All these ligands confer higher conformational rigidity on the chelate rings formed due to the presence of aromatic or oxazoline substituents in the metallacycle.

For the majority of cases, the higher the enantioselectivity of the reaction in the presence of a complex, the larger is the molecular volume of the chirality-determining substituent in the conformationally rigid chelate ring of the complex (only the most efficient substituents are listed in Table 7).

If a chiral centre is located at the donor atom of the ring, as in the case of the ligands **103**–**105**, the coordination of the ligand by the metal atom results in the formation of two stereoisomeric complexes.

Scheme 3

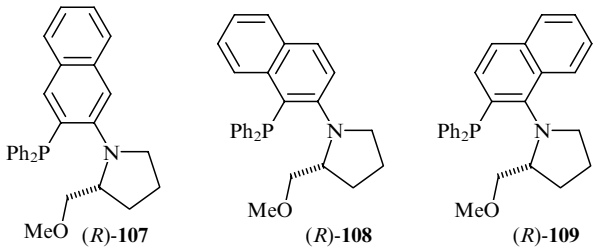




Ligand	*ee* (%)	Product configuration	Ref.
(*R*,*S*)-**103**	6	*S*	214
(*S*)-**104**	36	*S*	215
(*R*)-**105**	49	*R*	215
(*R*)-**106**	85	*R*	216

The substituents in such stereoisomers can fall into octants bearing opposite signs; therefore, it is expected that the reaction enantioselectivity cannot be too high, which is the case. However, the introduction of an additional substituent preventing free rotation around the C–N bond (ligand **106**) causes a sharp increase in the enantioselectivity.

A similar situation is observed for complexes with the ligands **107**–**109**.[215]



Ligand	*ee* (%)	Product configuration
(*R*)-**107**	24	*R*
(*R*)-**108**	39	*R*
(*R*)-**109**	74	*R*

The arrangement of the naphthyl rings in the ligand **109** hinders the free rotation of the pyrrolidine fragment to the largest extent if compared with compounds **107** and **108**; therefore, the enantioselectivity of the reaction is higher in this case.

Bidentate ligands of the cyclophane [217] and ferrocene [218] series have been described, which appear to be too bulky to allow the analysis of the octant projections of the complexes based on them.

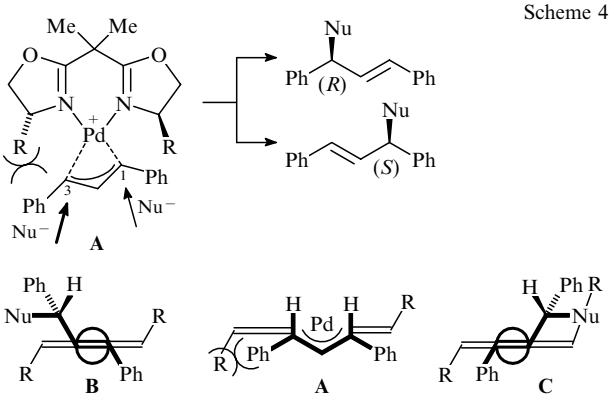
The enantioselectivity of the allylic alkylation catalysed by conformationally rigid palladium complexes depends only slightly on reaction conditions. For example, the *ee* value of the reaction product formed in the presence of the Pd–**84** complex depends only slightly on the nature of the cation in MOAc.[198] The enantioselectivity is virtually independent of either the precursor of the catalytic complex and the solvent or of temperature and reaction time.

Some ligand complexes provide sufficiently high reaction enantioselectivity, but their octant projections are difficult to establish for a number of reasons. For some complexes containing bulky tetradentate C_2-symmetric,[72, 73, 219–223] tridentate asymmetric [72, 196, 224] and tetradentate asymmetric [225] ligands, X-ray diffraction data are lacking. Complexes with some bi- and tridentate ligands [194, 216, 226, 227] manifest rotational isomerism as in the case of the ligands **103**–**109**. Bi-, tri- and tetradentate C_1- and C_2-symmetric ligands of some other complexes [221, 224, 225, 228–236] have too bulky backbones and determination of their octant projections is ambiguous.

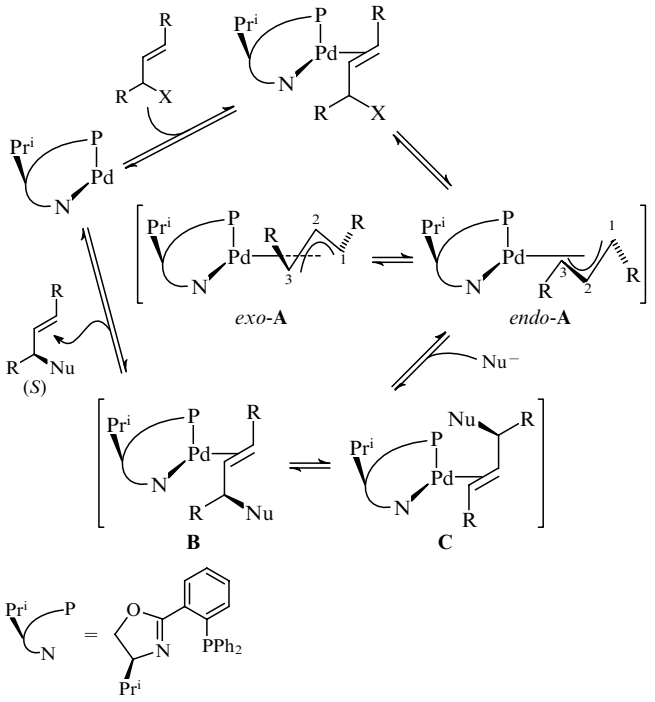
The mechanism of allylic alkylation includes oxidative addition of the allylic group to a Pd(0) complex to yield diastereomeric π-allylic intermediates (see Schemes 2 and 3), which are at equilibrium (the π–δ–π-mechanism), and their subsequent attack by a nucleophile from the side opposite to the coordinated palladium.[75, 171, 185, 237–239] The irreversible oxidative addition of the allylic group occurs much faster than the nucleophilic attack. The rate of the epimerisation of π-allylic intermediates is also by one or two orders of magnitude higher.[237] Therefore, the attack by a nucleophile is the limiting and, simultaneously, the asymmetric induction step. The latter is controlled by an asymmetric π-allylic intermediate irrespective of whether the starting palladium complex is asymmetric or chiral C_2-symmetric. The predominant enantiomer of the reaction product, which determines its configuration,[237] is formed *via* a π-allylic intermediate, which is in excess.

An alternative opinion[75, 185] consists of the following: if the starting complex is chiral and C_2-symmetric, the enantiomerism of the major product is determined by the competition between the positions C(1) and C(3) of the coordinated allylic substituents subject to the attack by the nucleophile in a single reaction intermediate. This is exemplified by the complex Pd–(*R*)-**70** (Scheme 4). The square-planar geometry of this intermediate was confirmed by X-ray diffraction analysis.[185] The intermediates

Scheme 4



Scheme 5



of reactions catalysed by other palladium complexes have similar structures.[174, 200, 240–242] The enantioselectivity is determined by the regioselectivity of the nucleophilic attack on the (1,3-diphenylallyl)palladium intermediate at positions C(3) or C(1). X-Ray diffraction and ^{13}C NMR spectroscopic data suggest that the Pd–C(3) bond is longer than the Pd–C(1) bond, presumably due to the steric interaction of the allylic phenyl group at the C(3) atom with the neighbouring benzyl group (R) in the dihydroxazole ring of the ligand **70**. The elongation of the bond increases the reactivity of the allylic substituent at position C(3) and favours its attack by the nucleophile at this position. The configuration of the reaction product [*ee* = 88% (*R*)] is consistent with this interpretation. Analogous considerations were employed in the analysis of reactions with other chiral C_2-symmetric complexes.[75] However, the concept of the regioselective activation of palladium–allylic bonds differs from that suggesting that the enantioselectivity is determined by the direct interaction of the chiral ligand with the nucleophile.[243–247]

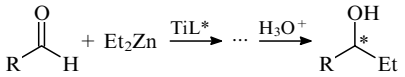
An alternative interpretation of enantioselectivity is based on the differences in the thermodynamic stabilities of the Pd(0) complexes **B** and **C** with the product the existence of which was recently confirmed experimentally (see Scheme 4).[238] As regards stereochemistry, the intermediate **B**, which favours the formation of the (*R*)-product, is undoubtedly more stable than the intermediate **C**.

If asymmetric complexes contain different donor atoms as in, *e.g.*, the complex Pd–**83**, two (1,3-diphenylallyl)palladium intermediates are in equilibrium.[238] The catalytic cycle of the allylic alkylation reaction catalysed by the Pd–**83** complex [R = Ph, X = OAc, Nu = $CH(CO_2Me)_2$] is shown in Scheme 5. The attack by the nucleophile at positions C(1) or C(3) of the intermediates *exo*-**A** and *endo*-**A** corresponds to the four possible reaction routes two of which, *viz.*, the attack at position C(3) of the intermediate *exo*-**A** and at position C(1) of the intermediate *endo*-**A**, should yield the *S*-enantiomer, which is the case. The intermediate **B** was identified experimentally by NMR spectroscopy,[238] therefore, it it assumed that the predominant reaction route involves a nucleophilic attack at the *trans*-position relative to the phosphorus atom in the intermediate *exo*-**A**. This conclusion is in keeping with the allylic alkylation mechanism proposed for reactions catalysed by other asymmetric palladium complexes.[178, 200, 239–248]

Thus, the asymmetric induction in the allylic alkylation catalysed by palladium chiral C_2-symmetric complexes takes place either in the step of the chiral intermediate, which has lost its C_2-symmetry after coordination to the substrate (see Scheme 4, intermediate **A**), or during the conversions of chiral intermediates (see Scheme 5) which are also devoid of the symmetry elements (except for C_1). In this case, palladium complexes containing both chiral C_2-symmetric ligands and chiral C_1-symmetric (asymmetric) ligands ensure high (up to 98%–99%) enantioselectivity of this reaction.

VI. Alkylation of benzaldehyde with dialkylzinc catalysed by titanium complexes

The formation of optically active alcohols in reactions of aldehydes with diethylzinc at low temperatures in the presence of *in situ* generated titanium chiral complexes is a well-studied reaction.[9, 17, 249, 250]



The reaction of benzaldehyde with diethylzinc in the presence of titanium complexes with chiral diols, sulfonamides and phosphoramides has been studied in especially great detail (Table 8). The experimental results suggest that the regularities Pr^{oct}–(*R*), Mr^{oct}–(*S*) and *Pr*–(*R*), *Mr*–(*S*) are fulfilled with a probability of 97%.

The same probability of fulfilment (87%) of the dependences based on the use of octant and quadrant projections [Pr^{oct}–(*S*), Mr^{oct}–(*R*) and *Pr*–(*S*), *Mr*–(*R*)] was also observed in the alkylation of benzaldehyde with diethylzinc in the presence of titanium asymmetric complexes with amino alcohols, *N*-sulfonylamino alcohols and *N*-thiophosphoramido alcohols (Table 9).

A hypothetical catalytic cycle of alkylation of benzaldehyde with diethylzinc in the presence of titanium complexes with *N*-substituted diamines is shown in Scheme 6.[266] Presumably, the intermediate **A** is the key species. This reacts with the aldehyde to give dialkoxytitanate **B**, which regenerates the key intermediate **A** in such a way that the catalytic cycle is closed. According to this scheme, the asymmetric induction takes place in the interaction of the aldehyde with the asymmetric complex irrespective of the symmetry (C_1 or C_2) of the starting catalytic complex. The maximum values of *ee* for the alkylation of benzaldehyde catalysed by Ti complexes with chiral C_2- and C_1-symmetric ligands are nearly identical (up to 98%).

Table 8. Asymmetric alkylation of benzaldehyde (**S**) with diethylzinc in the presence of titanium complexes with chiral diols, sulfonamides and phosphoramides.

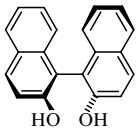
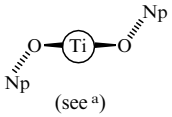
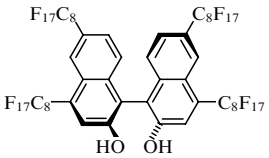
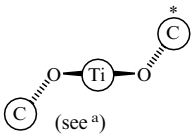
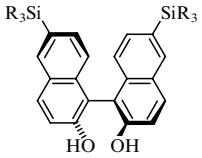
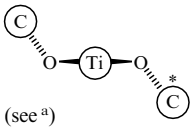
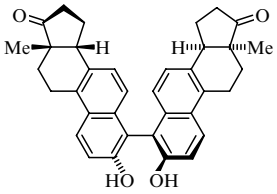
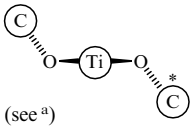
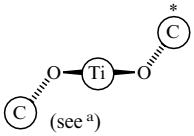
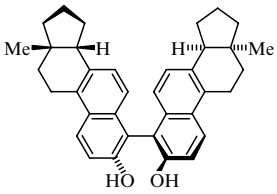
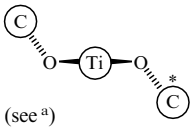
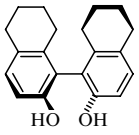
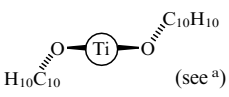
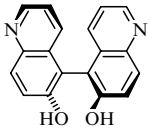
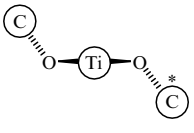
Ligand (complex)	Molar ratio of reaction components	T /°C	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (configuration of 1-phenylpropan-1-ol)	Ref.
					Pr^{oct}/Mr^{oct}	Pr/Mr		
Complexes with chiral C_2-symmetric ligands								
 (*S*)-**110**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.2 : 1.4 : 3	−78	 (see [a])	RR(−), RL(−)	Mr^{oct}	Mr	95.6 (*S*) 85 (*S*)	252 253
 (*S*)-**111**	$Ti(OPr^i)_4$: L = = 1 : 0.2	45	 (see [a])	RR(−), RL(−)	Mr^{oct}	Mr	58 (*S*)	254
 (*R*)-**112** (R = $(CH_2)_2C_6F_{13}$)	L : Et_2Zn : : $Ti(OPr^i)_4$: **S** = = 0.2 : 3 : 1.2 : 1	0	 (see [a])	RR(+), RL(+)	Pr^{oct}	Pr	83 (*R*)	255, 256
 (*R*)-**113**	**S** : Et_2Zn : : $Ti(OPr^i)_4$: L = = 1 : 1.9 : 1.4 : 0.2	−20	 (see [a])	RR(+), RL(+)	Pr^{oct}	Pr	78 (*R*)	257
(*S*)-**113**	**S** : Et_2Zn : : $Ti(OPr^i)_4$: L = = 1 : 1.9 : 1.4 : 0.2	−20	 (see [a])	RR(−), RL(−)	Mr^{oct}	Mr	82 (*S*)	257
 (*R*)-**114**	**S** : Et_2Zn : : $Ti(OPr^i)_4$: L = = 1 : 1.9 : 1.4 : 0.2	−20	 (see [a])	RR(+), RL(+)	Pr^{oct}	Pr	57 (*R*)	257
 (*S*)-**115**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.2 : 1.4 : 3	0	 (see [a])	RR(−), RL(−)	Mr^{oct}	Mr	98.5 (*S*)	258
 (*R*)-**116**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.2 : 1.4 : 3	0		RR(+), RL(+)	Pr^{oct}	Pr	89 (*R*)	259

Table 8 (continued).

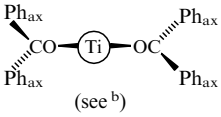
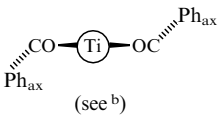
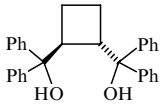
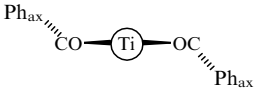
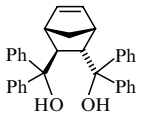
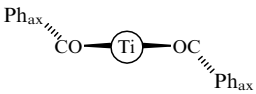
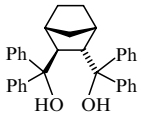
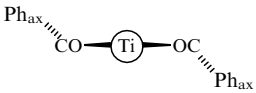
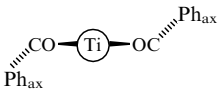
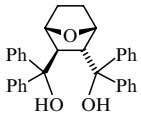
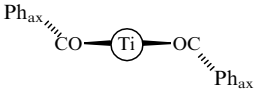
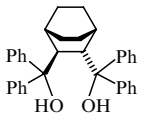
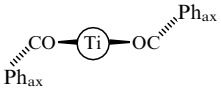
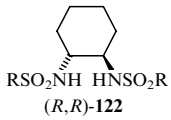
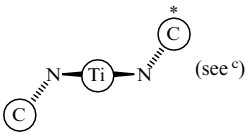
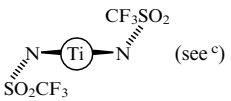
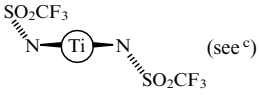
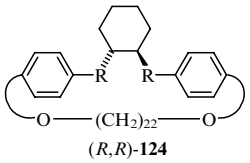
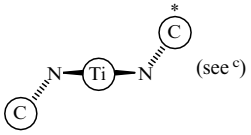
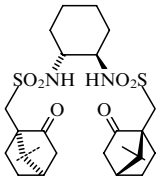
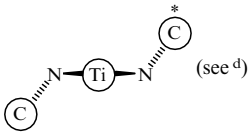
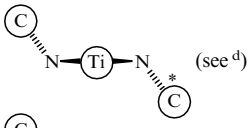
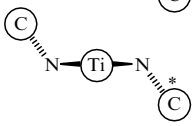
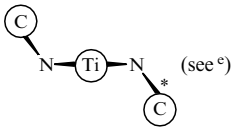
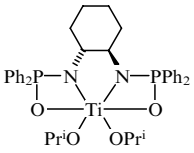
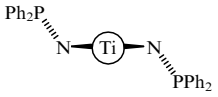
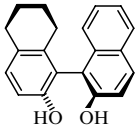
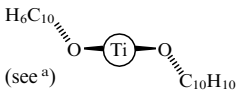
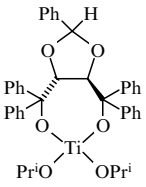
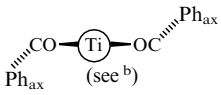
Ligand (complex)	Molar ratio of reaction components	T /°C	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (configuration of 1-phenylpropan-1-ol)	Ref.
					Pr^{oct}/Mr^{oct}	Pr/Mr		
Complexes with chiral C_2-symmetric ligands								
$Ti[(R,R)$-**41**$]_2$	**S** : Et_2Zn : : $Ti[(R,R)$-**41**$]_2$ = = 1 : 1.8 : 1.2	0	 (see [b])	RR(−), RL(−), FR(−), FL(−)	Mr^{oct}	Pr	90 (*R*)	107
$Ti(OPr^i)_2[(R,R)$-**41**]	**S** : Et_2Zn : : $Ti(OPr^i)_4$: : $Ti(OPr^i)_2[(R,R)$-**41**] = = 1 : 1.8 : 1.2 : 0.2	0	 (see [b])	RR(−), RL(−)	Mr^{oct}	Pr	98 (*S*)	107
 (*S*,*S*)-**117**	**S** : Et_2Zn : : $Ti(OPr^i)_4$: : [Ti/L] = = 1 : 1.8 : 1.2 : 0.2	−25		RR(+), RL(+)	Pr^{oct}	Pr	88 (*R*)	260
 (*S*,*S*)-**118**	**S** : Et_2Zn : : $Ti(OPr^i)_4$: : [Ti/L] = = 1 : 1.8 : 1.2 : 0.2	−25		RR(+), RL(+)	Pr^{oct}	Pr	60 (*R*)	260
 (*S*,*S*)-**119**	**S** : Et_2Zn : : $Ti(OPr^i)_4$: : [Ti/L] = = 1 : 1.8 : 1.2 : 0.2	−25		RR(+), RL(+)	Pr^{oct}	Pr	70 (*R*)	260
(*R*,*R*)-**119**	$Ti(OPr^i)_4$: L = = (1.2 − 1.4) : 0.2	−78 to −20		RR(−), RL(−)	Mr^{oct}	Mr	98 (*S*)	261, 262
 (*S*,*S*)-**120**	**S** : Et_2Zn : : $Ti(OPr^i)_4$: : [Ti/L] = = 1 : 1.8 : 1.2 : 0.2	−25		RR(+), RL(+)	Pr^{oct}	Pr	70 (*R*)	260
 (*R*,*R*)-**121**	$Ti(OPr^i)_4$: L = = (1.2 − 1.4) : 0.2	−78 to −20		RR(−), RL(−)	Mr^{oct}	Mr	82 (*S*)	261, 262
 (*R*,*R*)-**122** (R = 4-$MeOC_6H_4$)	**S** : $Ti(OPr^i)_4$: : Et_2Zn : L = = 1 : 1.2 : 1.2 : 0.02	−45	 (see [c])	RR(−), RL(−)	Mr^{oct}	Mr	98 (*S*)	264
 (*R*,*R*)-**123**	**S** : $Ti(OPr^i)_4$: : Et_2Zn : L = = 1 : 1.2 : 1.2 : 0.02	−30	 (see [c])	RR(−), RL(−)	Mr^{oct}	Mr	99 (*S*)	265
(*S*,*S*)-**123**	**S** : $ZnEt_2$: : $Ti(OPr^i)_4$: L = = 1 : 1.2 : 0.048 : 0.04	0	 (see [c])	RR(+), RL(+)	Pr^{oct}	Pr	98 (*R*)	266

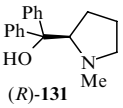
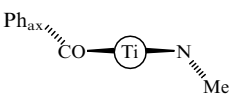
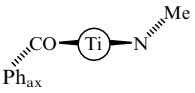
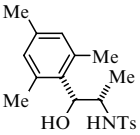
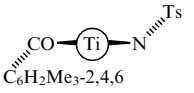
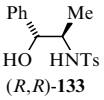
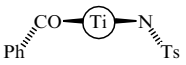
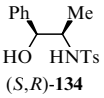
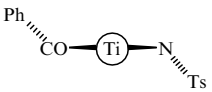
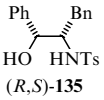
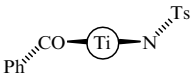
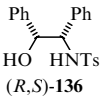
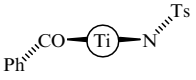
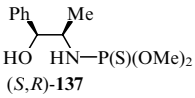
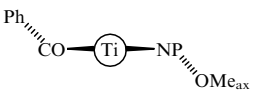
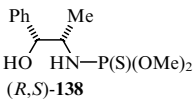
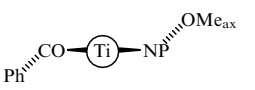
Table 8 (continued).

Ligand (complex)	Molar ratio of reaction components	T /°C	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (configuration of 1-phenylpropan-1-ol)	Ref.
					Pr^{oct}/Mr^{oct}	Pr/Mr		
Complexes with chiral C_2-symmetric ligands								
 (R,R)-**124** (R = $NHSO_2$)	**S** : $Ti(OPr^i)_4$: : Et_2Zn : L = = 1 : 1.2 : 1.2 : 0.02	−45	 (see [c])	RR(−), RL(−)	Mr^{oct}	Mr	89 (*S*)	264
 (R,R)-**125**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.2 : 1.4 : 3	−20	 (see [d])	RR(−), RL(−)	Mr^{oct}	Mr	91 (*S*)	267
(S,S)-**125**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.2 : 1.4 : 3	−20	 (see [d])	RR(+), RL(+)	Pr^{oct}	Pr	57 (*R*)	267
 (S,S)-**126**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.01 : 1.2 : 1.2	−40		RR(+), RL(+)	Pr^{oct}	Pr	98 (*R*)	268
 (R,R)-**127** (R = C_6H_2-3,5-Cl_2-2-OH)	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.2 : 1.4 : 1.8	−23	 (see [e])	FR(−), FL(−)	Mr^{oct}	Pr	99 (*S*)	269, 270
 (R,R)-**128**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.2 : 1.4 : 1.8	−50 to −20		RR(+), RL(+)	Pr^{oct}	Pr	81 (*R*)	271
Complexes with asymmetric ligands								
 (*R*)-**129**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.2 : 1.4 : 3	0	 (see [a])	RR(+), RL(+)	Pr^{oct}	Pr	91 (*R*)	272
 (R,R)-**130**	**S** : Et_2Zn : : $Ti(OPr^i)_4$: : $Ti(OPr^i)_2$[(R,R)-**130**] = 1 : 1.8 : 1.2 : 0.2	−20	 (see [b])	RR(−), RL(−)	Mr^{oct}	Mr	98 (*R*)	107

[a] X-Ray diffraction data (see Ref. 251). [b] X-Ray diffraction data (see Ref. 107). [c] X-Ray diffraction data (see Ref. 263). [d] X-Ray diffraction data (see Ref. 267). [e] Calculation (see Ref. 269).

It is of note that the feasibility of the configurational model (Pr^{oct}/Mr^{oct} or Pr/Mr) in the alkylation of benzaldehyde in the presence of titanium complexes with various chiral C_1- and C_2-symmetric ligands is very high (up to 93%). This testifies to a similarity of the reaction mechanisms in both cases and corrobo-

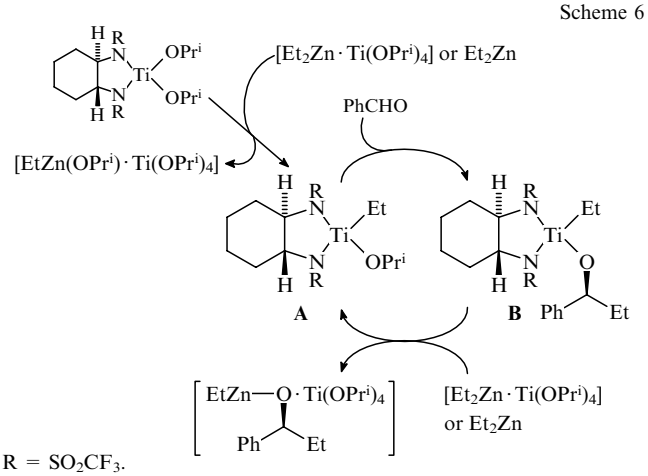
Table 9. Asymmetric alkylation of benzaldehyde (**S**) with diethylzinc in the presence of titanium asymmetric complexes with amino alcohols, *N*-sulfonylamino alcohols and *N*-phosphorothioamido alcohols.

Ligand	Molar ratio of reaction components	T /°C	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (product configuration)	Ref.
					Pr^{oct}/Mr^{oct}	Pr/Mr		
 (*R*)-**131**	**S** : L : $Ti(OPr^i)_4$: : $(cyclo\text{-}C_3H_5)_2Zn$ = = 1 : 0.05 : 1.2 : 3	−18		RR(+), RL(+)	Pr^{oct}	Pr	84 (*S*)[a]	273
(*S*)-**131**	**S** : L : $Ti(OPr^i)_4$: : $(cyclo\text{-}C_3H_5)_2Zn$ = = 1 : 0.2 : 1.2 : 3	0		RR(−), RL(−)	Mr^{oct}	Mr	86 (*R*)[a]	273
 (*R*,*S*)-**132**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.05 : 1.2 : 2	0		RR(−), RL(−)	Mr^{oct}	Mr	84 (*S*)[b]	274
 (*R*,*R*)-**133**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.05 : 1.2 : 2	0		RR(+), RL(−)	Pr^{oct}/Mr^{oct}	Mr/Pr	0	274
 (*S*,*R*)-**134**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.05 : 1.2 : 2	0		RR(+), RL(+)	Pr^{oct}	Pr	83 (*S*)[b]	274
 (*R*,*S*)-**135**	20 mol.% [L], 1 mmol $Ti(OPr^i)_4$	0		RR(−), RL(−)	Mr^{oct}	Mr	>99 (*R*)[b]	275
 (*R*,*S*)-**136**	10 mol.% [L], 0.5 mmol $Ti(OPr^i)_4$	0		RR(−), RL(−)	Mr^{oct}	Mr	90 (*R*)[b]	275
 (*S*,*R*)-**137**	**S** : L : $Ti(OPr^i)_4$: : Et_2Zn = = 1 : 0.05 : 1.5 : 1.5	−30		RR(+), RL(+)	Pr^{oct}	Pr	97 (*S*)[b]	276
 (*R*,*S*)-**138**	**S** : L : $Ti(OPr^i)_4$: : $(cyclo\text{-}C_3H_5)_2Zn$ = = 1 : 0.15 : 1.2 : 3	−30		RR(−), RL(−)	Mr^{oct}	Mr	96 (*R*)[a]	273

[a] The reaction product is cyclo-$C_3H_5CH(OH)Ph$. [b] The reaction product is 1-phenylpropan-1-ol.

rates the conclusion that the maximum enantioselectivity of this reaction does not depend on the symmetry of the ligand.

Scheme 6



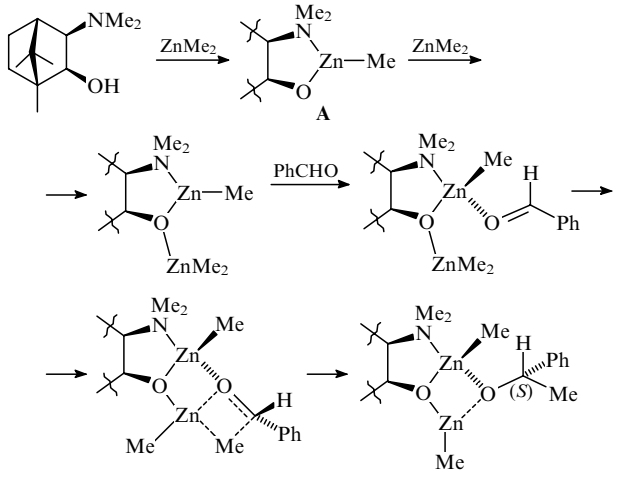
R = SO_2CF_3.

VII. Alkylation of benzaldehyde with dialkylzinc in the presence of amino alcohols and related compounds

In the asymmetric alkylation of aldehydes with dialkylzinc (see Refs 9, 17, 249 and 250), chiral amino alcohols, amido alcohols, diamines, diols, amino thiols, disulfides and diselenides represented components of *in situ* generated catalytic systems. The reaction of benzaldehyde with diethylzinc is a standard reaction, but in this case it is carried out in the absence of $Ti(OPr^i)_4$. As can be judged from the number of compounds tested as chiral ligands, this reaction seems to be a leader among other asymmetric reactions.

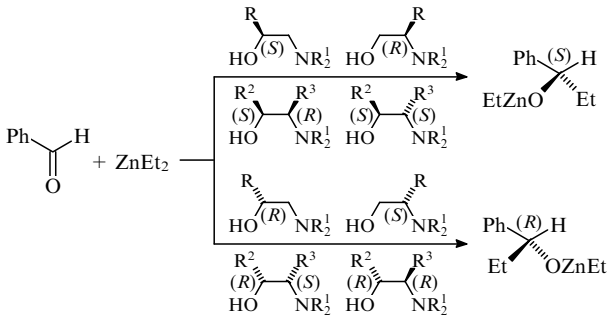
Experimental and theoretical studies into the mechanism of the reaction of dialkylzinc with benzaldehyde in the presence of amino alcohols have made it possible to establish the order of formation of intermediates [3, 9, 277–281] (Scheme 7). The first step includes the formation of the chelate zinc complex **A** with an amino alcohol, which determines the stereochemistry of its further conversions. The configurational relationships between the

Scheme 7



amino-alcohol ligand and the reaction product are described by the scheme (Scheme 8) proposed by Noyori *et al.*[249]

Scheme 8



This scheme is based on a large body of experimental evidence [282–344] and reflects adequately the relationship between the product and ligand configurations. A comparison of configurational models for the reaction of dialkylzinc with benzaldehyde in the presence of amino alcohols,[304–316, 333] which provide the maximum enantioselectivity of the reaction, is given in Table 10. The data from Table 10 and the analysis of experimental data [282–344] suggest that the regularities $Pr^{oct} \rightarrow (S)$, $Mr^{oct} \rightarrow (R)$ and $Pr \rightarrow (S)$, $Mr \rightarrow (R)$ are equally observed in nearly 93% of cases. However, in contrast to the octant model, the quadrant

Table 10. Alkylation of benzaldehyde with diethylzinc catalysed by *in situ* generated zinc complexes with chiral (bidentate) amino alcohols.

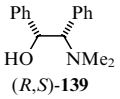
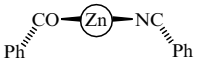
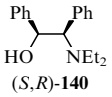
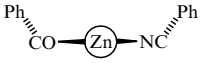
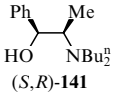
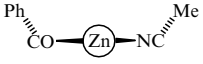
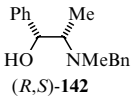
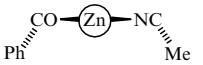
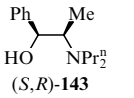
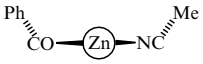
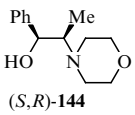
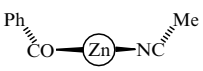
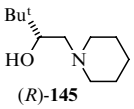
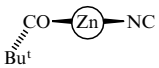
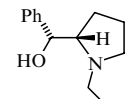
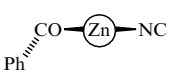
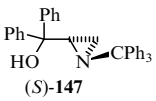
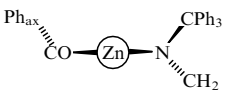
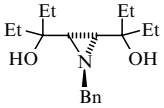
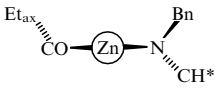
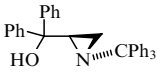
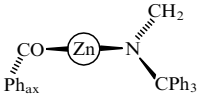
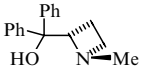
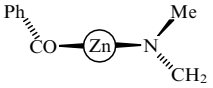
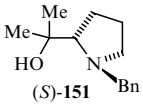
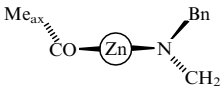
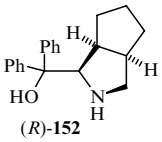
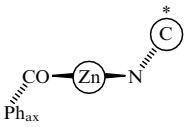
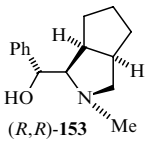
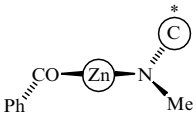
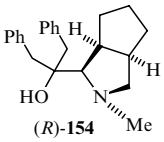
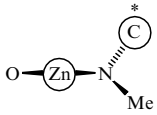
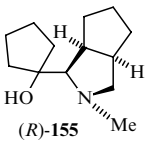
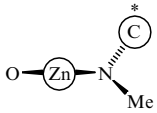
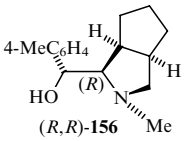
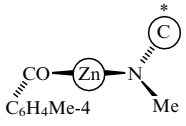
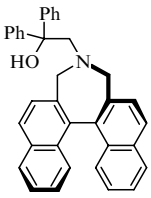
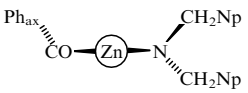
Ligand (complex)	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (product configuration)	Ref.
			Pr^{oct}/Mr^{oct}	Pr/Mr		
 (*R*,*S*)-**139**		RR(+), RL(−) [a]	$\sum Mr^{oct}$	*Mr*	97 (*R*)	282
 (*S*,*R*)-**140**		RR(−), RL(+) [a]	$\sum Pr^{oct}$	*Pr*	94 (*S*)	283
 (*S*,*R*)-**141**		RR(−), RL(+) [a]	$\sum Pr^{oct}$	*Pr*	90 (*S*)	283–286
 (*R*,*S*)-**142**		RR(+), RL(−) [a]	$\sum Mr^{oct}$	*Mr*	86 (*R*)	287
 (*S*,*R*)-**143**		RR(−), RL(+) [a]	$\sum Pr^{oct}$	*Pr*	92 (*S*)	288
 (*S*,*R*)-**144**		RR(−), RL(+) [a]	$\sum Pr^{oct}$	*Pr*	88 (*S*)	288
 (*R*)-**145**		RL(−)	Mr^{oct}	*Mr*	98 (*R*)	282
 (*R*,*S*)-**146**		RL(−)	Mr^{oct}	*Mr*	100 (*R*)	289
 (*S*)-**147**		RR(+), RL(+), FR(+)	Pr^{oct}	*Pr*	99 (*S*)	301, 302

Table 10 (continued).

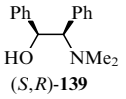
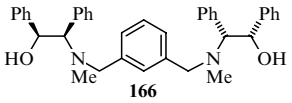
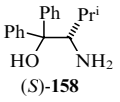
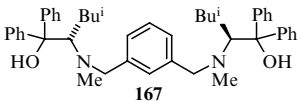
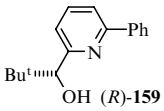
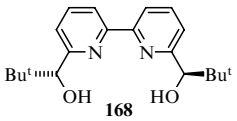
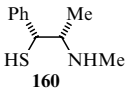
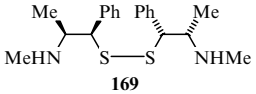
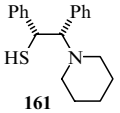
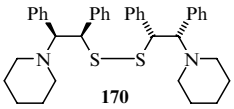
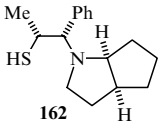
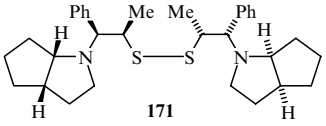
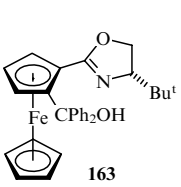
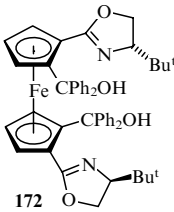
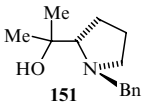
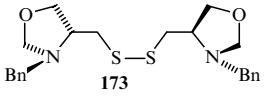
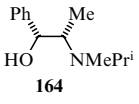
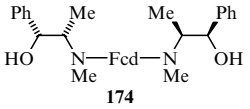
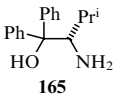
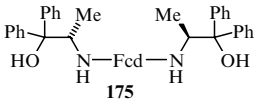
Ligand (complex)	Schematic projection of metallacycle	Location of chirality-determining substituents in octants	Chirality in configurational models		*ee* (%) (product configuration)	Ref.
			Pr^{oct}/Mr^{oct}	Pr/Mr		
 (*S*,*S*)-**148**		RR(+), RL(+), FR(+)	Pr^{oct}	Pr/Mr	94 (*S*)	303
 (*R*)-**149**		RR(−), RL(−), FR(−)	Mr^{oct}	Mr/Pr	99 (*R*)	302
 (*S*)-**150**		RR(+), RL(+), FR(+)	Mr^{oct}	Pr/Mr	98 (*S*)	304
 (*S*)-**151**		RR(+), RL(+), FR(+)	Pr^{oct}	Pr/Mr	99 (*R*)	305
 (*R*)-**152**		RR(−), RL(−)	Mr^{oct}	*Mr*	99 (*R*)	306–312
 (*R*,*R*)-**153**		RR(−), RL(−), FR(−)	Mr^{oct}	Mr/Pr	68 (*R*)	306–312
 (*R*)-**154**		RR(−), RL(−)	Mr^{oct}	Mr/Pr	90 (*R*)	306–312
 (*R*)-**155**		RR(−), FR(−)	Mr^{oct}	Mr/Pr	99 (*R*)	306–312
 (*R*,*R*)-**156**		RR(−), RL(−), FR(−)	Mr^{oct}	Mr/Pr	91 (*R*)	306–312
 (*S*)-**157**		FR(+), RR(+), RL(+)	Pr^{oct}	Pr/Mr	87 (*S*)	318

Note. The sign $\sum$ designates the predominant contribution of the given type of chirality. [a] A substituent at the left senior atom has preference.

projection model can be applied to a limited number of ligands only. The quadrant model is inapplicable to reactions in the presence of complexes with the ligands **148**–**151** and **153**–**157** due to location of coordinated ligand fragments in the quadrants with opposite signs.

Here, as in other cases (see, *e.g.*, Tables 3–7), the overwhelming majority of complexes that ensure high enantioselectivity of the reaction possess conformational rigidity. These include five-membered chelate complexes with bulky substituents (Ph, Bu^t, Pr^i) the conformational rigidity of the chelate ring which is

Table 11. Asymmetric alkylation of benzaldehyde with diethylzinc catalysed by 'monomeric' chiral C_1-symmetric and 'dimeric' C_2-symmetric ligands (toluene, 20 °C).

'Monomeric' ligand	*ee* (%) (product configuration)	Ref.	'Dimeric' ligand	*ee* (%) (product configuration)	Ref.
 (*S*,*R*)-**139**	73 (*S*)	282	 **166**	75 (*S*)[a]	355
 (*S*)-**158**	88 (*R*)	290	 **167**	87 (*R*)[a]	355
 (*R*)-**159**	93 (*R*)	320, 321	 **168**	97 (*R*)	320, 321
 **160**	80 (*R*)	345 – 347	 **169**	86 (*R*)	345 – 347
 **161**	99 (*R*)	348 – 350	 **170**	99 (*R*)	348 – 350
 **162**	90 (*R*)	306	 **171**	86 (*R*)	306
 **163**	93 (*R*)	338, 342, 343	 **172**	91 (*R*)	342
 **151**	99 (*R*)	305	 **173**	> 99 (*R*)	356
 **164**	80 (*R*)	286	 **174**	70 (*R*)	357
 **165**	88 (*R*)	290	 **175**	83 (*R*)	357

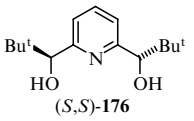
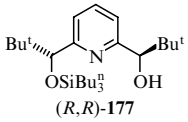
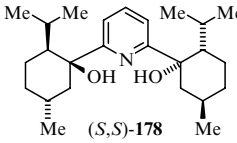
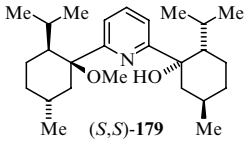
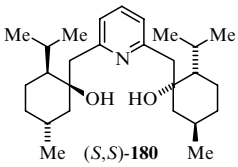
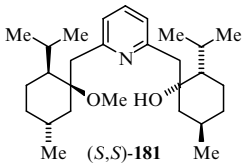
[a] This reaction occurs in the presence of 4-ClC_6H_4CHO.

provided by a more advantageous equatorial position of the substituent [77] (complexes with the ligands **139** – **145**). The conformational rigidities of many efficient complexes are enhanced owing to the incorporation of one of the bonds of the first chelate ring into the second ring (complexes with the ligands **146** – **156**). Complexes with atropoisomeric ligands (*e.g.*, the ligand **157**) constitute a special group.

Octant projections can be constructed for a small group of complexes with chiral amino thiols, which represent thio analogues of the ligands **139** – **143** and **145**.[306, 326, 345 – 354] All of them have the same structural features as the amino alcohol-containing complexes. It is therefore not surprising that reactions catalysed by these complexes follow the same regularities, *viz.*, $Pr^{oct}\rightarrow(S)$, $Mr^{oct}\rightarrow(R)$ and $Pr\rightarrow(S)$, $Mr\rightarrow(R)$, with a high degree of probability (~90%).

A comparison of chiral C_2-symmetric tetradentate ligands (which are rather few in number) (Table 11) with their asymmetric 'monomeric' bidentate counterparts has shown that the involvement of all these ligands in the reaction is largely due to the involvement of their 'monomeric' asymmetric fragments. A comparison of the experimental results obtained with the complexes with both 'monomeric' and the corresponding 'dimeric' ligands revealed a virtually complete coincidence of the *ee* values and the

Table 12. Asymmetric alkylation of benzaldehyde with diethylzinc in the presence of chiral C_2-symmetric tridentate ligands and their asymmetric analogues.[358]

Chiral C_2-symmetric ligand	*ee* (%) (product configuration)	Asymmetric ligand	*ee* (%) (product configuration)
 (*S*,*S*)-**176**	65 (*S*)	 (*R*,*R*)-**177**	67 (*R*)
 (*S*,*S*)-**178**	55 (*S*)	 (*S*,*S*)-**179**	35 (*S*)
 (*S*,*S*)-**180**	93 (*S*)	 (*S*,*S*)-**181**	95 (*S*)

product configurations, which provides convincing evidence in favour of this conclusion.

An analysis of the data summarised in Table 12, which compares the results obtained in the presence of chiral C_2-symmetric tridentate ligands and their asymmetric analogues, corroborated this conclusion. The similarity of the *ee* values and the coincidence of the product configurations were observed in the majority of cases. This provides additional evidence in favour of the fact that the reaction in the presence of chiral C_2-symmetric tri- and tetradentate ligands involves their asymmetric bidentate fragments.

Thus, it is only asymmetric ligands that are effective in the asymmetric alkylation of benzaldehyde with diethylzinc in the absence of $Ti(OPr^i)_4$.

Successful implementation of asymmetric reactions in the presence of chiral C_2-symmetric ligands requires the presence of $Ti(OPr^i)_4$ in the catalytic system (see Table 8).

Unfortunately, the applicability of the above-described regularities to a large number of complexes cannot be estimated because their octant projections are too difficult to establish.

In some cases,[359–365] the problem arises as to whether the chiral centre is located in the side chain of the ligand or the complex contains a ring spiro-fused to the metallacycle.[319,366–373] Because of the ambiguity of determination of the octant projection, complexes with bulky tri- and tetradentate ligands cannot be considered.[362,368,371,374–388] However, the tetradentate C_2-symmetric ligands **166**–**175** were included in Table 11, because there is evidence that their bidentate fragments are involved in the catalysis as components of the corresponding complexes. For complexes with ligands containing bulky fragments[306,383] that rotate around the C–C bond in their side chains, the octant projection cannot be established at all. Complexes with several seven-membered metallacycles[389–392] contain $(CH_2)_2$ fragments, and their octant projections cannot be unambiguously determined because of the conformational lability of the coordinated ligand. The octant projections of the complexes the ligands in which form eight-membered (and larger-sized) metallacycles[393,394] as well as of some other complexes[285,372,376,395–397] cannot be reliably determined either.

The mechanism of asymmetric induction in the alkylation of benzaldehyde with diethylzinc in the presence of chiral C_2-symmetric ligands will be discussed in the next Section.

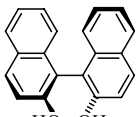
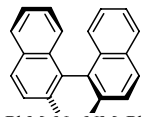
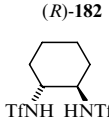
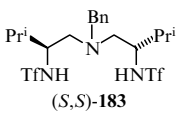
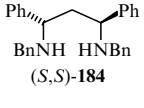
VIII. Complexes with chiral C_2-symmetric ligands as the asymmetry inductors

Previously, it was concluded[6] that the intermediate responsible for the asymmetric induction in some asymmetric reactions is asymmetric irrespective of the symmetry of the starting complex. This conclusion was made in the analysis of mechanisms of such reactions as hydrogenation of amino acid precursors and hydrosilylation of ketones in the presence of chiral metal complexes. In other words, in the catalysis by complexes containing C_2-symmetric ligands the C_2-symmetry is lost in the step preceding the asymmetric induction. High enantioselectivity can be achieved with the use of complexes with both asymmetric and chiral C_2-symmetric ligands as catalysts. A similar conclusion was made in the analysis of allylic alkylation, cyclopropanation, the Diels–Alder reactions and benzaldehyde alkylation with dialkylzinc on titanium complexes.

Complexes with chiral C_2-symmetric and asymmetric ligands manifest different efficiencies in the hydrogen-transfer hydrogenation of acetophenone and hydroformylation of styrene. Complexes with asymmetric ligands provide higher enantioselectivities (see Sections III and IV). Presumably, this can be related to the C_2-symmetry of the intermediate responsible for the asymmetric induction (in the case of chiral C_2-symmetric complexes).

The presence or the absence of titanium complexes in the catalytic system influences significantly the enantioselectivity of the alkylation of benzaldehyde with dialkylzinc in the presence of chiral C_2-symmetric ligands (Table 13). In all the cases studied,

Table 13. Asymmetric addition of diethylzinc to benzaldehyde in the presence of chiral C_2-symmetric ligands and complexes of $Ti(OPr^i)_4$ with these ligands.

In the absence of $Ti(OPr^i)_4$			In the presence of $Ti(OPr^i)_4$		
Ligand	*ee* (%) (product configuration)	Ref.	Ligand	*ee* (%) (product configuration)	Ref.
 (*S*)-**110**	no reaction	253	(*S*)-**110**	92 (*S*)	253
 (*R*)-**182**	8 (*R*)	339	–	–	–
 (*R*,*R*)-**123**	54 (*S*)	266, 267, 268	(*R*,*R*)-**123**	99 (*S*)	266, 267, 269
 (*S*,*S*)-**183**	15 (*S*)[a]	398	(*S*,*S*)-**183**	72 (*S*)[b]	398
 (*S*,*S*)-**184**	15[c] 0[d]	399 399	– –	– –	– –

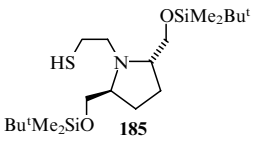
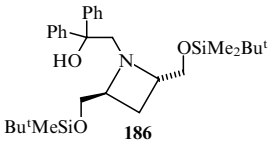
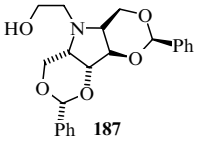
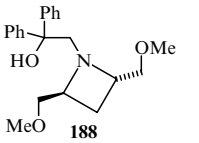
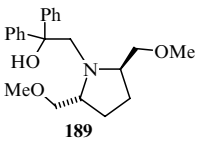
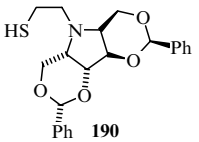
[a] In the presence of molecular sieves MS 4 Å. [b] The reaction with 4-$CF_3C_6H_4CHO$. [c] The configuration is not indicated. [d] The reaction with 4-MeC_6H_4CHO.

the enantioselectivity is highly enhanced in the presence of $Ti(OPr^i)_4$ in the catalytic system.

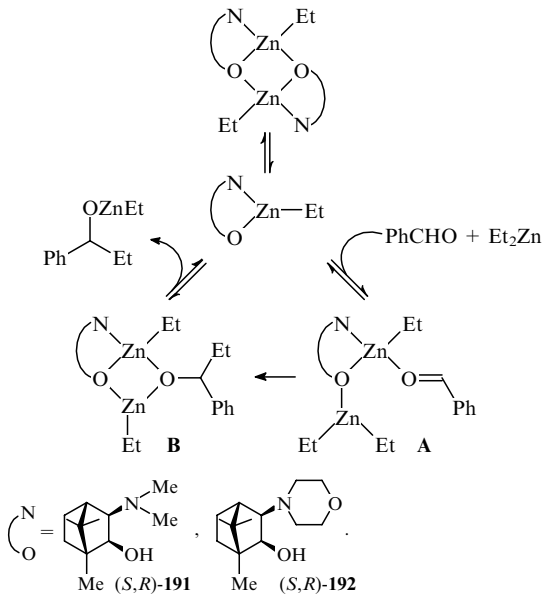
The data on the addition of diethylzinc to benzaldehyde in the presence of chiral ligands with a C_2-symmetry axis passing through the donor nitrogen atom are presented in Table 14. In C_2-symmetric fragments of the ligands **188**–**190**, one of the oxygen atoms can be coordinated with the catalyst (in contrast to the ligands **185** and **186** which are devoid of such an ability due to the shielding of the oxygen atoms by bulky groups). As a result, the *ee* value increases from 10(20)% to 90(95)% (the ligand **187** [400, 401] occupies an intermediate position). An analysis of molecular models revealed that the zinc atom can coordinate not only the donor atoms of the ligands [O(S) and N], but also the oxygen atom of one of two identical and C_2-symmetric groups in the nitrogen-containing ring. Under these conditions, the second group becomes inaccessible for the coordination. The C_2-symmetry of the catalytic complex is lost as a result of additional coordination of the oxygen atom of only one of the chiral C_2-symmetric groups of the ligand by the zinc atom. Complexes with similar ligands that are incapable of such coordination and therefore manifest higher symmetry appear to be less enantioselective as catalysts.

The reaction catalysed by chiral C_2-symmetric titanium complexes proceeds *via* the asymmetric intermediate **A** (see Scheme 7). Based on calorimetric studies, a catalytic model has been proposed for the reaction catalysed by complexes with asymmetric ligands of the type **191** and **192** (Scheme 9). According to this scheme, the asymmetric induction is realised in the **A** → **B** conversion step.

Table 14. Addition of diethylzinc to benzaldehyde in the presence of chiral ligands with a C_2-symmetry axis passing through the donor nitrogen atom.

Ligand	*ee* (%) (product configuration)	Ref.
 **185**	10 (*R*)	363
 **186**	20 (*S*)	361
 **187**	40 (*S*)	400, 401
 **188**	~90 (*S*)	361
 **189**	~90 (*R*)	362, 363
 **190**	95 (*S*)	400, 401

Scheme 9

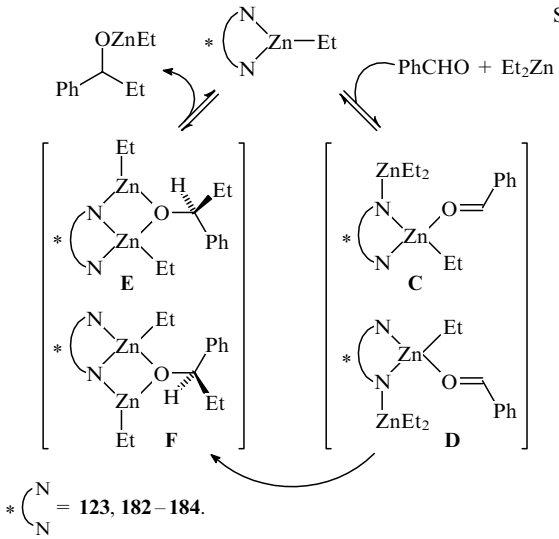


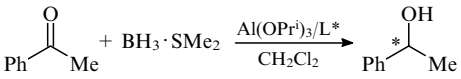
Extrapolation of this model to a reaction catalysed by complexes with chiral C_2-symmetric ligands of the type **123**, **182**–**184** (Scheme 10) demonstrates that in this case, too, the **A** → **B** step is responsible for asymmetric induction. The structures **C** and **D** determining the asymmetric induction are diastereomeric, but the immediate environments of the coordinated aldehyde in each of these intermediates represent enantiomeric species. Presumably, the difference in the concentrations of the diastereomers **E** and **F**, which favour the formation of different enantiomers of the reaction product, is small; therefore, the enantioselectivity of the reaction should be low which actually is the case.

Thus, the increase in enantioselectivity on going from a reaction in the presence of chiral C_2-symmetric ligands to a reaction catalysed by titanium complexes with these ligands (see Table 13), is due to the loss of C_2-symmetry by the intermediate. A deviation from this rule, which is manifested in moderate enantioselectivity in the presence of the chiral C_2-symmetric ligand **123** [*ee* = 54% (*S*)], can be attributed to the fact that the ideal C_2-symmetry is not realised in this case, presumably due to, *e.g.*, conformational distortions in the six-membered ring.

The reduction of acetophenone with borane in the presence of chiral C_2-symmetric atropoisomeric ligands becomes enantioselective upon the addition of $Al(OPr^i)_3$ to the reaction system (Table 15).[402]

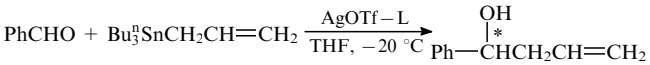
Scheme 10

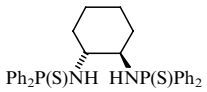
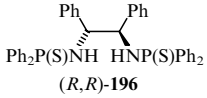
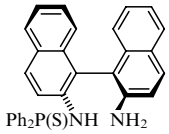




The enhancement of the enantioselectivity of this reaction can be due to the same factors as in the alkylation of benzaldehyde with dialkylzinc in the presence of $Ti(OPr^i)_4$ and without it (see Table 13). Apparently, in contrast to the chiral C_2-symmetric reducing reagent based on borane and a ligand, the catalytic system generated *in situ* from borane, a chiral C_2-symmetric ligand and $Al(OPr^i)_3$, is asymmetric.

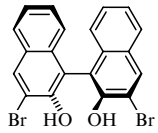
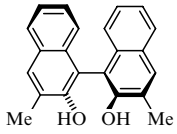
The loss of C_2-symmetry in the series of chiral ligands of the same type is accompanied by a drastic enhancement of the enantioselectivity of certain catalytic reactions. The allylation of aldehydes is an example.[403]

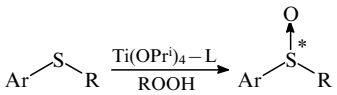


L	*ee* (%)	Product configuration
 (*R*,*R*)-**195**	9	*R*
 (*R*,*R*)-**196**	15	*R*
 (*R*)-**197**	52	*R*

The oxidation of sulfides is a striking example of high sensitivity of the enantioselectivity of a catalytic reaction to the C_2-symmetry of the chiral ligands.

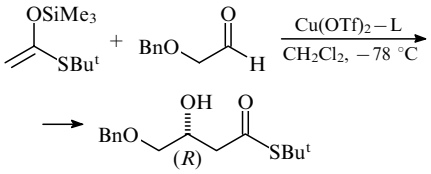
Table 15. Asymmetric reduction of acetophenone with borane catalysed by chiral C_2-symmetric ligands in the presence and in the absence of $Al(OPr^i)_3$ (CH_2Cl_2, 20 °C).[402]

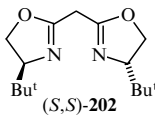
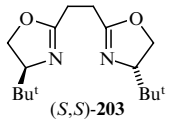
Ligand	Reaction in the absence of $Al(OPr^i)_3$		Reaction in the presence of $Al(OPr^i)_3$	
	yield (%)	*ee* (%)	yield (%)	*ee* (%)
(*R*)-**110**	78	0	97	60 (*S*)
 (*R*)-**193**	90	0	94	46 (*R*)
 (*R*)-**194**	93	0	97	10 (*R*)
(*R*)-**115**	91	0	95	71 (*S*)



As can be seen from Table 16, the enantioselectivity of this reaction depends on the structures of chiral diols as the ligands. A comparison of conformational rigidities of such ligands revealed that the possible conformational deviations from the ideal C_2-symmetry decrease in the following order: **198** < **199** ≪ **200** ≈ **201**. For the latter two ligands, the deviations are the greatest due to the free rotation of the Bu^t and Ph groups at the chiral carbon atoms around the C–C bond. This order coincides with the order of changes in *ee* of the reaction product formed in the presence of the same ligands (Table 16). Thus, in the sulfide oxidation these parameters are linearly interrelated.

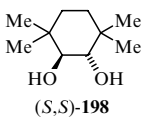
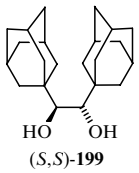
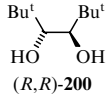
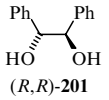
The existence of such a relationship is confirmed by an analysis of numerous published data on asymmetric catalytic reactions. Contrary to expectations, the transition from a conformationally labile six-membered metallacycle to a more rigid seven-membered ring results in a radical decrease in the enantioselectivity of aldol condensation.[407]



Ligand L	 (*S*,*S*)-**202**	 (*S*,*S*)-**203**
ee (%) (product configuration)	64 (*R*)	0

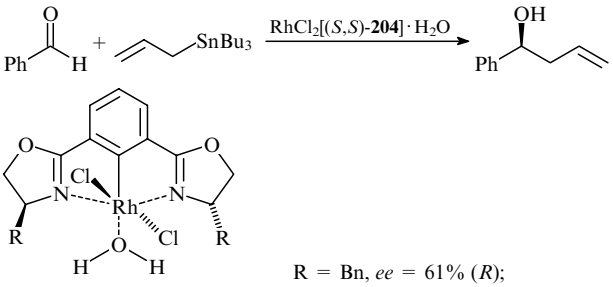
In this case, this can be attributed to a more perfect C_2-symmetry of the complex with a seven-membered metallacycle. Similarly, lower enantioselectivity of aldehyde allylation corre-

Table 16. Dependence of the enantioselectivity of oxidation of methyl *p*-tolyl sulfide and benzyl phenyl sulfide on the ligand structure.

Ligand (L)	Composition of reaction mixture and temperature	*ee* (%) (product configuration)		Ref.
		p-Tol–S–Me	Ph–S–Bn	
 (*S*,*S*)-**198**	$Ti(OPr^i)_4$–L, 4-$Pr^nC_6H_4O_2H$, MS 4Å, toluene, −20 °C	0	0	404
 (*S*,*S*)-**199**	$Ti(OPr^i)_4$–L, 4-$Pr^nC_6H_4O_2H$, MS 4Å, toluene, −20 °C	7 [a]	14 [a]	404
 (*R*,*R*)-**200**	$Ti(OPr^i)_4$–L, 4-$Pr^nC_6H_4O_2H$, MS 4Å, toluene, −20 °C	–	95 (*S*)	405
 (*R*,*R*)-**201**	$Ti(OPr^i)_4$–L, Bu^tO_2H, CCl_4, 0 °C	80 (*S*)	>99 (*S*)	406

[a] The configuration is not indicated.

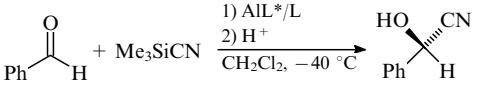
sponds to a more perfect C_2-symmetry of the complex $RhCl_2[(S,S)$-**204**$]\cdot H_2O$ (R = Ph) (in comparison with the symmetry of the same complex containing a benzyl substituent).[408]



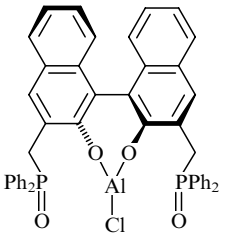
$RhCl_2[(S,S)$-**204**$]\cdot H_2O$

R = Bn, *ee* = 61% (*R*);
R = Ph, *ee* = 6% (*R*).

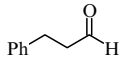
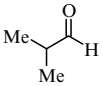
And, finally, there is evidence that the enhancement of enantioselectivity can be due to the loss, by the chiral C_2-symmetric catalytic complex, of the symmetry axis C_2. Numerous findings suggest that the enantioselectivity is enhanced upon addition of monodentate achiral auxiliary ligands (additives or co-catalysts) to the reaction mixture.[409] The cyanosilylation of aldehydes in the presence of Lewis acids as catalysts is a typical example of such a reaction.



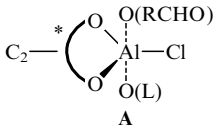
For example, the reaction catalysed by the aluminium complex AlCl[(*S*)-**205**] in the presence of an achiral ligand proceeds with a much higher enantioselectivity.[410]



AlCl[(*S*)-**205**]

Substrate				
Achiral ligand L	without ligand	$Bu_3P(O)$	without ligand	$Bu_3P(O)$
ee (%) (product configuration)	9 (*S*)	97 (*S*)	25 (*S*)	90 (*S*)

It is known that the intermediate **A**, which has the structure of a trigonal bipyramid, is formed in the presence of an achiral ligand.[411, 412]

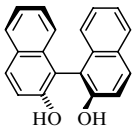
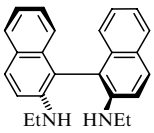
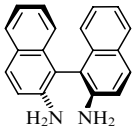
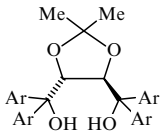
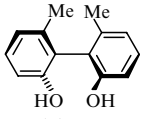


A

In contrast to the complex formed in the absence of an additional ligand, in the intermediate **A** the symmetry axis C_2 is lost. Consequently, the enhancement of the enantioselectivity can be explained by the asymmetry of the intermediate **A**. A similar effect in the Mannich reaction is induced by an additional ligand.[413] A weaker effect is observed in the allylic alkylation reaction,[414] *etc.*[415] upon introduction of an achiral ligand. Numerous examples of the use of molecular sieves (MS 4 Å) for enhancement of the enantioselectivity of a catalytic reaction in the presence of chiral C_2-symmetric metallocomplexes are known (for more recent publications, see Refs 416 and 417). This effect can also be due to the loss of the C_2-symmetry by chiral C_2-symmetric complexes upon chemisorption on the surface of aluminosilicate. As a result, the asymmetric induction is realised in the step involving the asymmetric intermediate, *i.e.*, that devoid of any symmetry elements other than C_1.

Thus, the opinion[418] that chiral C_2-symmetric ligands are the most efficient asymmetry inductors should probably be considered in the context of a concrete reaction mechanism. For example, in such reactions as hydrogen-transfer hydrogenation of ketones, hydroformylation of styrene or alkylation of aldehydes with dialkylzinc [without the involvement of $Ti(OPr^i)_4$ or analogous complexes], these ligands are less efficient than asymmetric ligands. In reactions like sulfide oxidation, complexes with a chiral C_2-symmetric ligand act as asymmetry inductors, most probably due to the deviation from the ideal C_2-symmetry. Actually, in such cases it is the intermediate that becomes asymmetric due to the loss of the symmetry axis C_2 that is responsible for the asymmetric induction.

The abnormal inefficiency of complexes with chiral C_2-symmetric ligands as asymmetry inductors was observed earlier, *e.g.*, in hydroformylation reactions.[170] This was rationalised by the peculiarities of this reaction, but the true reason for this phenomenon seems to be more fundamental. Presumably, this effect is not confined to catalytic reactions only. Thus, our findings[419–421] and the results by other investigators[422–425] point to an abnormally low enantioselectivity of acetophenone reduction by lithium chiral dihydrides $[(O\ O)LiH_2]$¶ modified by the atropoisomeric ligands **41**, **110**, and **206**–**208**.

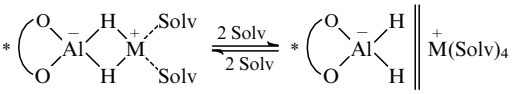
Ligand	*ee* (%) (product configuration)	Ref.	Ligand	*ee* (%) (product configuration)	Ref.
 (*R*)-**110** (binol)	2 (*R*) 0	422 420	 (*R*)-**208**	43 (*R*)	423
 (*R*)-**206**	9 (*R*)	423	 (*R*,*R*)-**41** (Ar = H, C_6H_4OMe-4)	78 (*R*)	425
 (*R*)-**207**	2 (*R*)	424			

Since the aluminium atom in $LiAlH_4$ has a tetrahedral environment, the structure of the dihydride anion based on these chiral C_2-symmetric ligands is close to ideal C_2-symmetric. The introduction of an ethyl group into the ligand **206** (giving the ligand **208**) increases the deviation of its C_2 symmetry from the ideal in comparison with the ligands **110**, **206** and **207**. It is this factor that is responsible for the moderate enantioselectivity of the dihydride containing the ligand **208**. Further enhancement of the enantioselectivity is observed upon transition to the ligand **41**,

¶ It was suggested[422] that the disproportionation of $Li(binol)AlH_2$ to $LiAlH_4$ and $LiAl(binol)_2$ was the reason for the low enantioselectivity of the reduction of ketones with this dihydride. Our experiments[420] showed that this was not the case: no disproportionation took place under the reaction conditions.

which has four phenyl groups that rotate around the $C-C_{Ph}$ bond and thus disturb the C_2-symmetry.

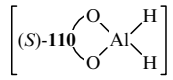
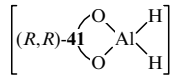
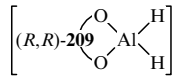
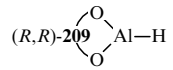
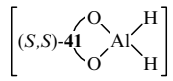
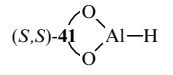
Both the non-modified hydrides $LiAlH_4$ and $NaAlH_4$ and diol-modified hydrides react with ketones in THF or diglyme, predominantly as contact and dissociated ion pairs.[426]



Solv is solvent.

Since the Li^+ cation is a stronger acid than Na^+, it can be expected that the bridging ring is more rigid in the case of Li; therefore, the violation of the C_2-symmetry in the case of lithium dihydride is less pronounced. In turn, the ring formed by the ligand in a planar monohydride based on AlH_3 is more strained than that in the dihydride based on $NaAlH_4$. Therefore, the C_2-symmetry of the latter is less perfect. We found that the *ee* values of the reduction products of substrates containing C=O and C=N groups are higher in the case where the C_2-symmetry of the hydride is violated to a greater extent [the ligand **209** represents an analogue of the ligand **41** (Ar = C_6H_4OMe-4)] (Table 17).

Table 17. Enantioselectivity in reduction with aluminium hydrides.[420, 421]

Substrate	Complex with aluminium hydride	Cation	*ee* (%)	Product configuration
PhCOMe		Na	38	(*S*)
		Li	0	–
PhCMe ‖ NP(O)Me_2		Na	78	(*R*)
		Li	30	(*R*)
PhC(O)Pr^i		Na	73	(*S*)
		–	7	(*S*)
		Na	76	(*R*)
		–	36	(*R*)

These data suggest that this phenomenon is versatile and is not confined to catalytic reactions.

IX. Conclusion

A comparison of the configurational models Mr^{oct}/Pr^{oct} and Mr/Pr, in the example of catalytic hydrogen-transfer hydrogenation, hydroformylation, allylic alkylation and alkylation of aldehydes with dialkylzinc and some other reactions, suggests that preference should be given to the former based on the octant projection.

The configurational relationships 'catalytic complex – reaction product' considered in this review are based on the analysis of octant and quadrant projections obtained from consideration of molecular models, X-ray diffraction data or calculations for certain structures. It is of note that both X-ray diffraction data and numerous calculations (to say nothing of molecular models) give purely probabilistic patterns of spatial arrangements of molecular fragments in real intermediates, especially under the reaction conditions. However, the accuracy of the estimation of the fulfillment of the regularity $Pr^{oct}-(S)$, $Mr^{oct}-(R)$ [or $Pr^{oct}-(R)$, $Mr^{oct}-(S)$] increases manifold with an increase in the number of variants under study. Having established such a regularity relative to a concrete substrate and a concrete reaction and knowing the configuration of the reaction product, its *ee* and reaction mechanism, one can get a better insight into the structure of an intermediate responsible for the asymmetric induction, especially if we take into consideration the fact that such an intermediate can be isolated and studied instrumentally in only a few catalytic reactions.

Thus, the judgement on the absolute configuration of the intermediate determining the asymmetric induction in the hydrogenation of enamides on rhodium bis(diphenylphosphine) complexes can be made exclusively by analogy with the structure of a stable diastereomeric intermediate present in excess in the reaction mixture. X-Ray diffraction analysis of the latter requires its preliminary isolation at low temperature,[427] *i.e.*, under the conditions where the ratio of the conformers changes drastically as can be evidenced from low-temperature circular dichroism data.[428] Moreover, the results of X-ray diffraction analysis of the complex in crystal from do not provide any relevant information about conformations of complexes in solution, since crystallisation forces are stronger than forces responsible for conformational changes. For example, the conformations of the ligand diop in crystals of the complexes Ir[(*S*,*S*)-(+)-diop](COD)Cl (see Ref. 429) and [(*R*,*R*)-(−)-diop]$NiCl_2$ (see Ref. 430) differ from the ideal twist-chair-λ and twist-chair-δ conformations which are more favourable. In the latter crystal, the distortions are so strong that the array of the phenyl groups determining the complex chirality becomes virtually symmetric with respect to the metal (the symmetry plane). If a complex retained such a conformation in solution in the asymmetric induction step, it would contradict the well-known rule of asymmetric catalysis ('no asymmetry without asymmetry'), since the cross-coupling in the presence of the same complex, [(*R*,*R*)-(−)-diop]$NiCl_2$, occurs enantioselectively.[431, 432]

It is of note that the interpretation of effects of metal complexes on the enantioselectivity in catalytic reactions using 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[433, 434] of the so-called chiral molecular recognition and induction is based on helical electronic effects in the chiral metallocomplex (catalyst) and the coordinating substrate. 'Handedness matching' of the signs of helical polarisability of a chiral catalyst and a coordinating substrate in enantioselective reactions should be met.

An optimistic prognosis of applicability of chiral C_2-symmetric compounds as asymmetry inductors has been made in the review[418] devoted to the phenomenon of asymmetric induction. The analysis made in the present review suggests that these prospects refer only to such reactions as enamide hydrogenation, allylic alkylation, alkylation with diethylzinc in the presence of $Ti(OPr^i)_4$ as well as cyclopropanation and the Diels–Alder reactions not considered in this review. It should also be noted that the use of the term 'chiral induction'[435] instead of the generally accepted term 'asymmetric induction' is incorrect, since the highest value of asymmetric induction is observed in the step of an asymmetric intermediate, *i.e.*, that devoid of any elements of symmetry (exception for C_1).

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