Russian Chemical Reviews **81** (9) 823 – 854 (2012) © 2012 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2012v081n09ABEH004305

Asymmetric induction in reactions catalyzed by metal complexes

V A Pavlov, T N Pavlova

Contents

I. Introduction 823
II. Asymmetric intermediates controlling asymmetric induction in the reactions involving complexes with C_2-symmetric chiral ligands 824
III. C_2-Symmetric intermediates controlling asymmetric induction in the reactions involving complexes with C_2-symmetric chiral ligands 835
IV. Enantioselectivity of reactions of substrates coordinated by one, two or three groups in the presence of complexes with C_2-, C_3- and D_2-symmetric chiral ligands 839
V. Dependence of the enantioselectivity of reactions catalyzed by C_2-symmetric complexes on additional achiral ligands and molecular sieves 845
VI. Comparison of the enantioselectivities of reactions in the presence of complexes of the same metal with C_2- and C_1-symmetric ligands of similar structure and under the same conditions 847
VII. Reactions catalyzed by complexes with asymmetric chiral ligands 848
VIII. Conclusion 850

Abstract. More than 250 asymmetric catalytic reactions with enantioselectivity approaching 100% are considered. The dependences of the enantiomeric excess of the product on the symmetries of the initial catalytic complex and the key intermediate that provides the asymmetric induction and on the number of coordinating functional groups in the substrate molecule are analyzed. Based on the catalytic cycles of asymmetric reactions proposed in the literature, two possible mechanisms of asymmetric induction are discussed, consecutive (stepwise) and cooperative (one-step) mechanisms. The bibliography includes 283 references.

I. Introduction

The last few years have seen 'intellectual outburst' in investigations of asymmetric catalytic reactions with enantioselectivity (enantiomeric excess of the product *ee*) approaching 100%. These reactions are catalyzed by metal complexes with chiral ligands. The dependence of enantioselectivity of such reactions on the symmetry (C_1, C_2 or C_3) of intermediate complexes (transition states) that control the asymmetric induction (key intermediates) has been analysed for monofunctional substrates.[1,2] It has been found out that reactions with high enantioselectivity (*ee* $\gg$ 60%) proceed only *via* C_1-symmetric (asymmetric) key intermediates when catalyzed by complexes with C_2- or C_3-symmetric ligands. The enantioselectivity of reactions with substrates possessing two or three coordinating groups reaches *ee* > 99% regardless of the symmetry of the catalytic complex.[1] The difference in the enantioselectivity of reactions with substrates that are coordinated by one or two (three) groups may be attributed to the minimum difference between the degrees of freedom (or free activation energy) of *proS*- or *proR*-coordination of substrate in the key intermediate in a monofunctional substrate. If the substrate is coordinated by two or three groups, the difference between the degrees of freedom or the activation energy of *proS*- and *proR*-coordination is much higher and, hence, the enantioselectivity is also higher. High enantioselectivity of reactions with such substrates has been revealed experimentally.[3,4] Indeed, in accordance with mechanisms proposed by Landis and Halpern [4] and Imamoto and co-workers,[5] the hydrogenation of amino acid precursors (three-point coordination) under the action of C_2-symmetric complexes proceeds *via* the formation of asymmetric key intermediate.[6]

Considering contemporary literature data and developing our hypotheses,[1–3] in the present review, we attempted to formulate and substantiate new concepts:

— the key intermediates responsible for asymmetric induction in highly enantioselective reactions must be asymmetric (in the case of C_2 symmetry of these intermediates, the enantioselectivity would not be high, *ee* < 60%);

— the mechanism of asymmetric induction may be one-step (cooperative) or two(three)-step (stepwise, consecutive);

— complexes with C_2-symmetric chiral ligands without additional achiral ligands (AAL) or molecular sieves cata-

V A Pavlov, T N Pavlova N D Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp. 47, 119991 Moscow, Russian Federation. Fax (7-499) 135 53 28,
e-mail: pvlv@ioc.ac.ru (V A Pavlov),
e-mail: pvlv69@mail.ru (T N Pavlova)

Received 28 February 2012
Uspekhi Khimii **81** (9) 823 – 854 (2012); translated by P A Nikitina

lyze the reactions with high enantioselectivity only for substrates capable of two- or three-point coordination;

— additional achiral ligands or molecular sieves in the reactions catalyzed by metal complexes with C_2-symmetric chiral ligands lead to the loss of C_2 symmetry by the key intermediate and, as a consequence, to the increase of enantioselectivity.

The order of consideration of reactions in the present review corresponds to the order of atomic numbers of metal catalysts. Here each reaction is considered for the substrate that has demonstrated the highest enantioselectivity.

II. Asymmetric intermediates controlling asymmetric induction in the reactions involving complexes with C_2-symmetric chiral ligands

1. Stepwise mechanism of asymmetric induction

The oxidative cross-coupling of 2-naphthols (*e.g.*, compounds **1** and **2** to give binaphthyldiol **3** possessing axial chirality) occurs in the presence of C_2-symmetric chiral dimeric iron complex with salan ligand **L1** (Scheme 1).[7]

Egami *et al.*[7] have proposed a possible catalytic cycle of this reaction (Scheme 2). According to this mechanism, the complex [FeOH(**L1**)]$_2$ loses C_2 symmetry upon the formation of key intermediates **A** and **B**. The asymmetric induction occurs in two steps: **A** → **B** → **C**.

Hydrovinylation of non-activated linear 1,3-dienes is catalyzed by [Co(**L2**)H]$^+$ (Schemes 3, 4).[8]

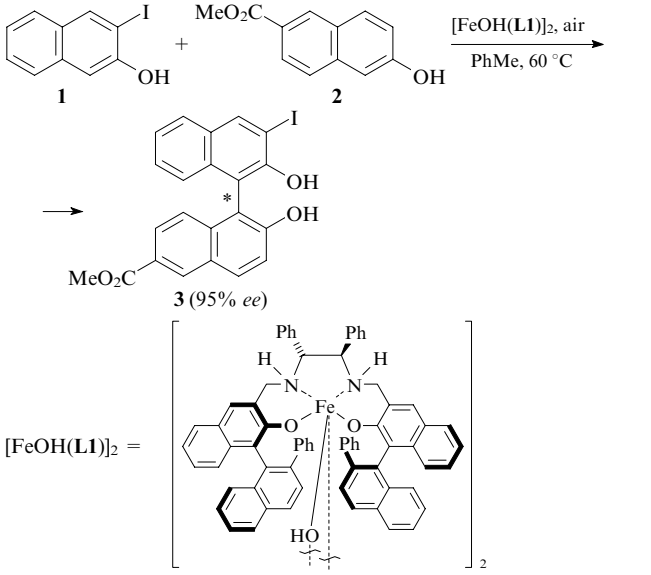
The proposed mechanism is given in Scheme 4.

The C_2-symmetric cobalt hydride complex loses symmetry upon the reaction with diene giving (*via* intermediate **A**) *syn-anti*-allyl cobalt intermediate **B**. It reacts with ethylene in the reaction mixture to give intermediate **C** and then intermediate **D** with an asymmetric carbon atom. Thus, the asymmetric induction happens in the consecutive steps **A** (**B**, **C**) → **D** (stepwise mechanism). Apparently, the replacement of the methyl group in the substrate by a considerably bulkier BnO(CH$_2$)$_2$ moiety will result in a more pronounced asymmetry of intermediate **C**. That is why, according to the hypothesis [1,2] of enantioselectivity increase on going from C_2- to C_1-symmetric key intermediate, such replacement is expected to increase the enantioselectivity. This agrees with experimental data.

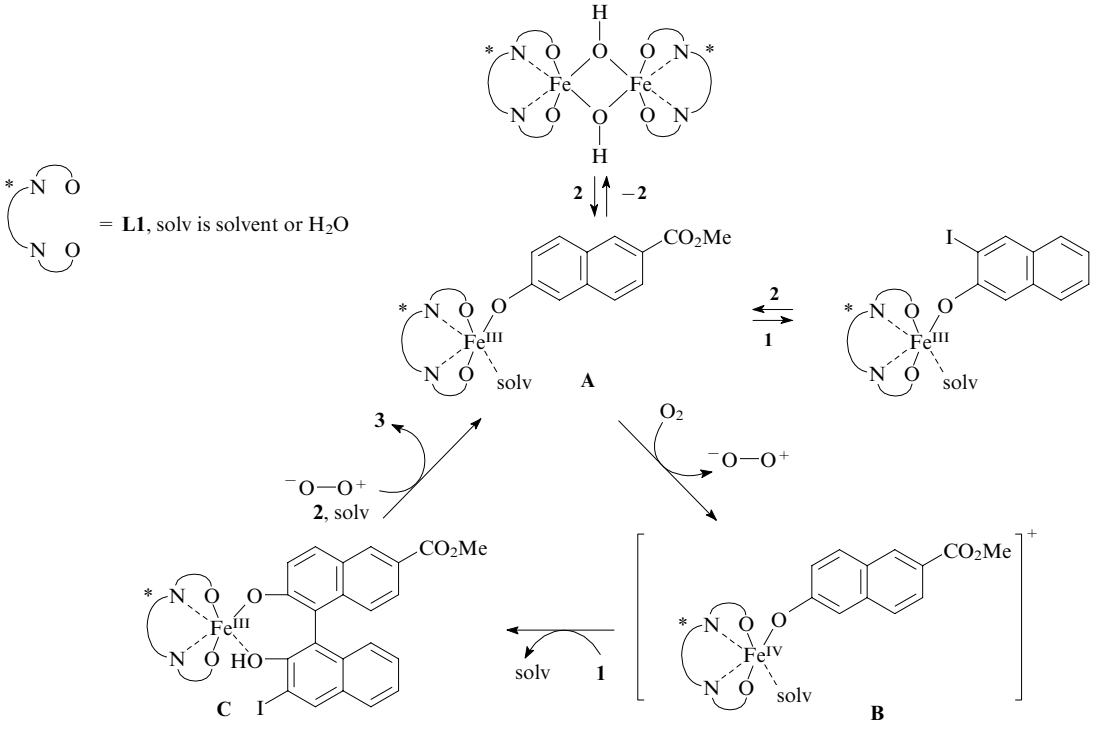
The enantioselective conjugate addition of α-ketoesters to nitroalkenes is catalyzed by [Ni(**L3**)(OAc)$_2$] (Scheme 5, hereinafter, rt stands for room temperature).[9]

Nakamura *et al.*[9] have proposed a sequence of reactions determining the asymmetric induction (Scheme 6). Obviously, asymmetric induction is realized in two steps *via* intermediates **A** and **B** (stepwise mechanism). The hypothesized key intermediate **A** is asymmetric. Unfortunately, the stereochemical role of triethylamine present in the reaction mixture is not reflected in this mechanism.

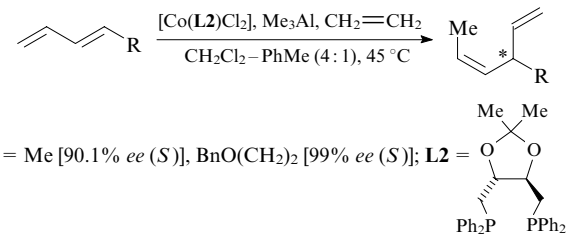
Scheme 1



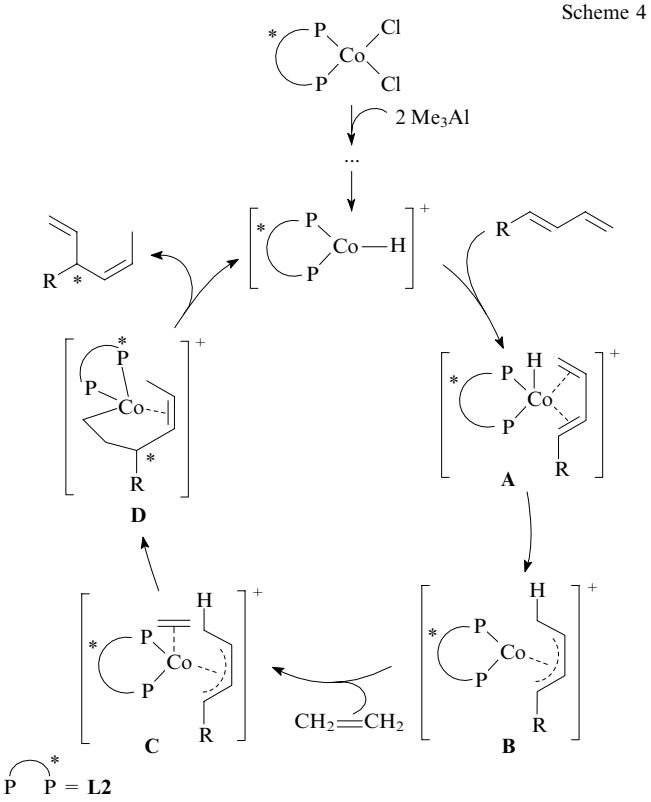
Scheme 2



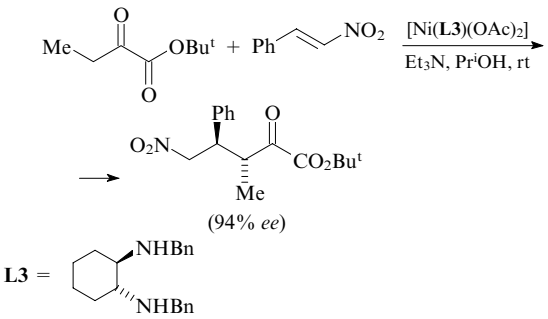
Scheme 3



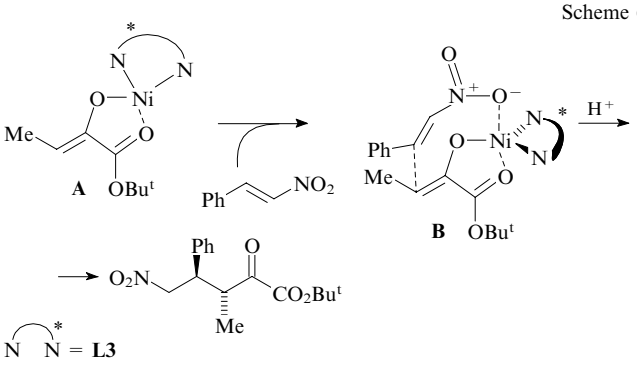
Scheme 4



Scheme 5

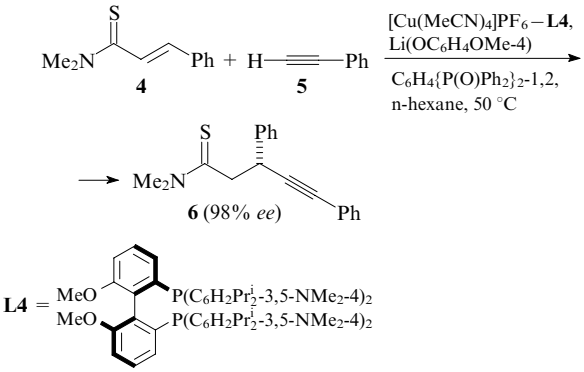


Scheme 6



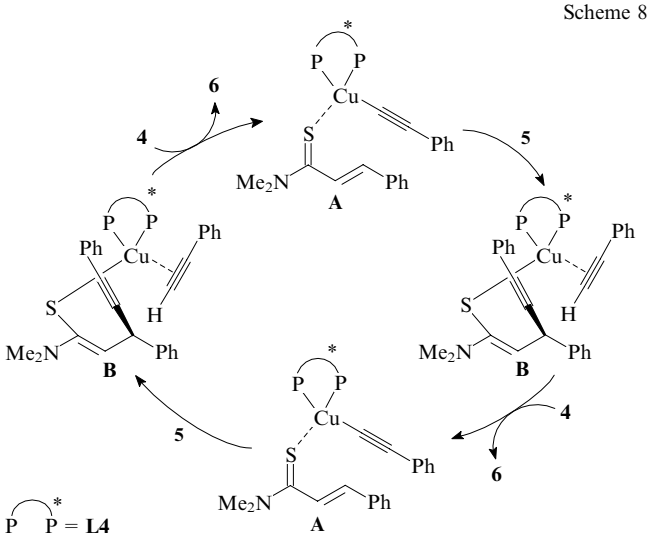
As an example of catalytic conjugate addition of terminal alkynes to α,β-unsaturated thioamides, consider the reaction of compounds **4** and **5**, resulting in product **6** (Scheme 7).[10] The reaction is catalyzed by Cu^{I} complex with chiral ligand **L4** in the presence of the AAL $C_6H_4\{P(O)Ph_2\}_2$-1,2.

Scheme 7



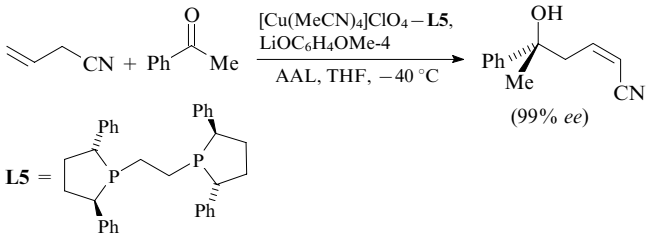
A possible mechanism of this reaction is presented in Scheme 8. In accordance with the proposed mechanism, the asymmetric induction occurs in stages **A** → **B** → **A**, where **A** is the asymmetric key intermediate. Thus, the mechanism of asymmetric induction may be classified as a stepwise one.

Scheme 8



A similar catalyst, namely, Cu^{I} complex with **L5** ligand, is also efficient in the γ-addition reaction of allyl cyanide to ketones, *e.g.*, to acetophenone (Scheme 9).[11]

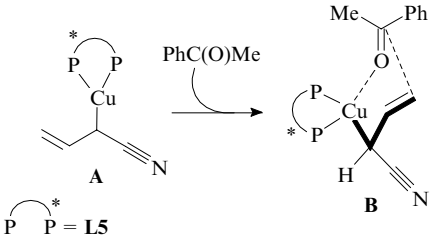
Scheme 9



According to the authors,[11] deprotonative activation of the ketone is the rate-determining step of the reaction (Scheme 10), the C_2 symmetry of the catalytic complex

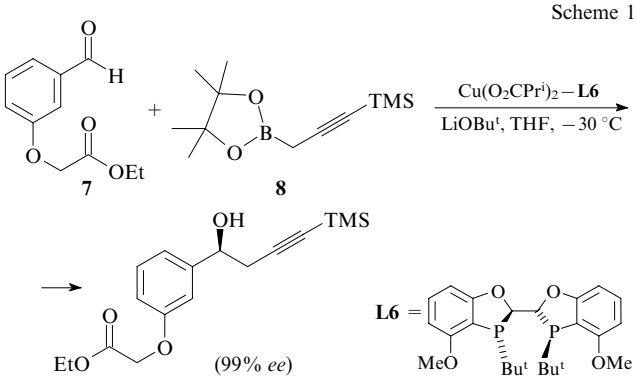
Cu–**L5** being lost upon the formation of intermediate **A**. The asymmetric induction proceeds in two steps *via* intermediates **A** and **B**. It should be noted that the coordinating additional achiral ligands [$C_6H_4\{P(O)Ph_2\}_2$-1,2 and $Ph_3P{=}O$] have no influence on the reaction enantioselectivity.

Scheme 10



Asymmetric propargylation of aldehydes (specifically, compound **7**) with propargylborolane **8** is catalyzed by chiral C_2-symmetric copper complex with **L6** (Scheme 11).[12]

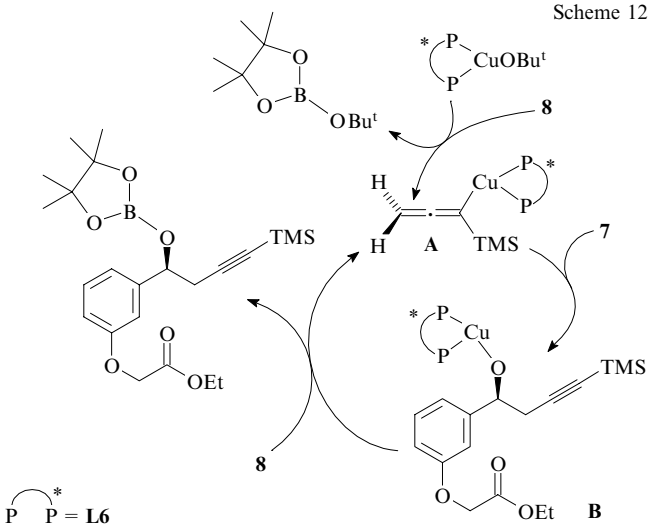
Scheme 11



TMS is trimethylsilyl

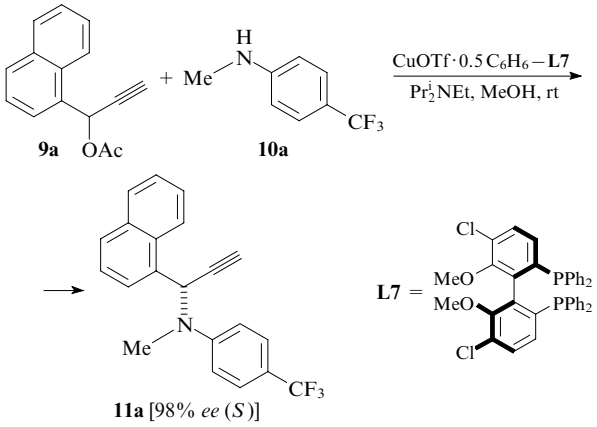
A catalytic cycle of this reaction has been proposed (Scheme 12). It is based on the interaction of chiral copper alkoxide with propargylborolane **8**, resulting in the formation of asymmetric intermediate **A**, which then reacts with aldehyde. Intermediate **B** with the asymmetric carbon atom undergoes borolane–Cu exchange, thus completing the catalytic cycle with the formation of the product and regeneration of chiral copper alkoxide. Thus, according to this mechanism, asymmetric induction proceeds in two steps *via* intermediates **A** and **B**.

Scheme 12

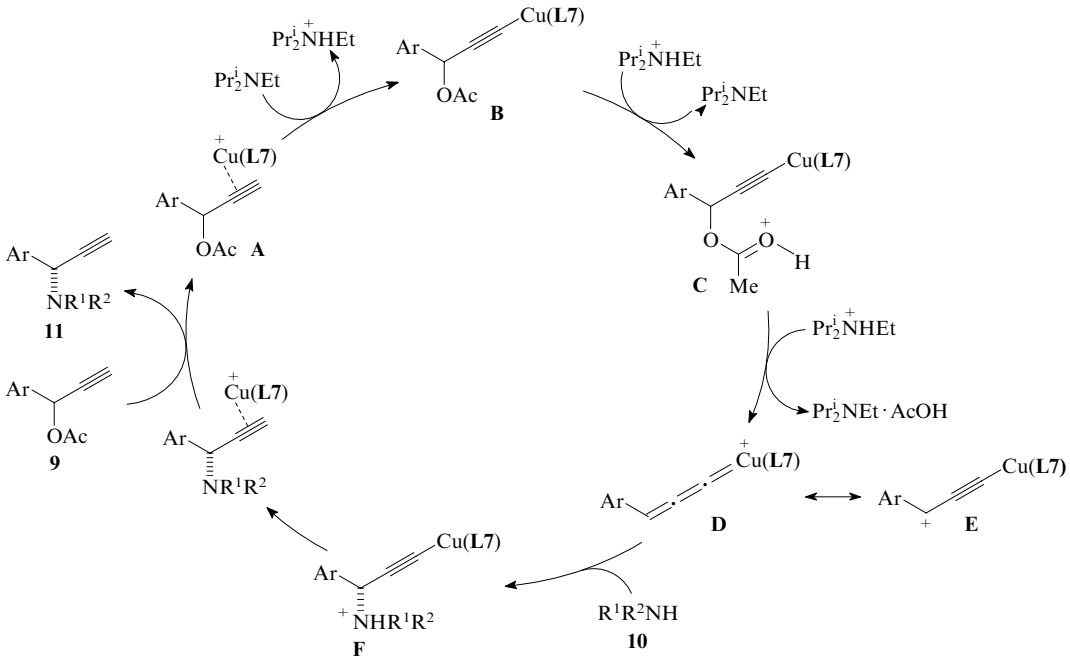


Hattori *et al.*[13] have studied the amination of propargylic esters **9** by amines **10** catalyzed by C_2-symmetric chiral

Scheme 13



Scheme 14

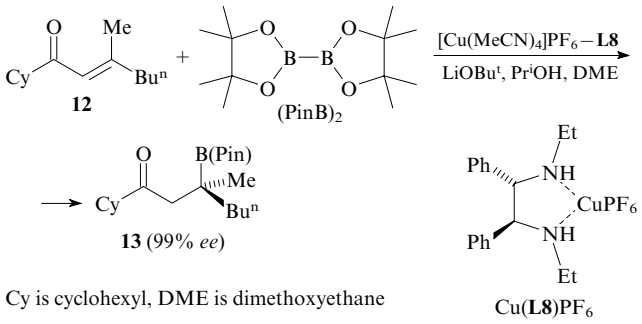


copper complex with ligand **L7**. As a result, chiral amines **11** were formed. The highest enantioselectivity was obtained in the reaction of compounds **9a** and **10a**, leading to product **11a** (Scheme 13). A possible reaction pathway is shown in Scheme 14.

Asymmetrtic Cu–allenylidene complex **D** is formed *via* the sequence of asymmetric intermediates **A**, **B**, **C**. Presumably, this complex is the key intermediate (its resonance form is Cu–acetylide complex **E**). According to this cycle, the asymmetric induction proceeds in several steps, which end with the step **D** → **F** (stepwise mechanism). However, the doubtfulness of this interpretation of asymmetric induction consists in the fact that the reaction centre giving rise to the asymmetric carbon atom (intermediate **F**) is remote from the chiral moiety [Cu(**L7**)].

Copper(I) complex with chiral secondary diamine **L8** catalyzes enantioselective conjugate boronation of β,β-disubstituted enones (*e.g.*, compound **12**) with bis(pinacolborane) [$(PinB)_2$], which leads to chiral alkylboronates (*e.g.*, compound **13**) (Scheme 15).[14]

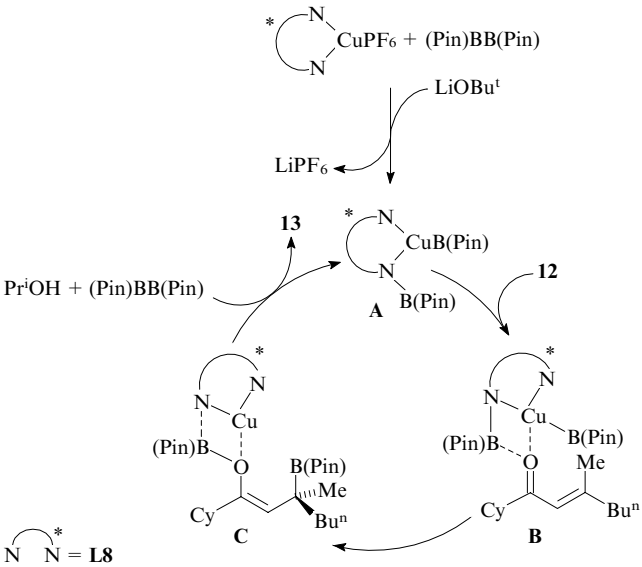
Scheme 15



Cy is cyclohexyl, DME is dimethoxyethane

A presumptive catalytic cycle of this reaction is presented in Scheme 16. After the formation of copper boryl intermediate **A**, the carbonyl oxygen atom of enone **12** is coordinated by the boron atom (the Lewis acid) of the aminopinaconyl boronate moiety of the catalyst to afford asymmetric key intermediate **B**. The next step of catalytic cycle leads to intermediate **C** with an asymmetric carbon atom. The formation of the product and the regeneration of complex **A** proceed *via* this intermediate upon its protonation by propan-2-ol. The proposed mechanism explains the low enantioselectivity of this reaction in the presence of ligand (*S*,*S*)-$Me_2NCH(Ph)CH(Ph)NMe_2$ (10% *ee*). Indeed, in this case the formation of N–B bond becomes impossible.

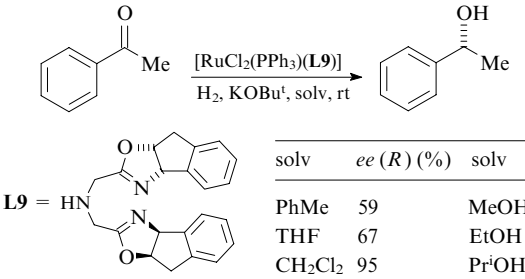
Scheme 16



Thus, in this reaction, asymmetric induction is realized in two consecutive steps *via* intermediates **A** and **B**.

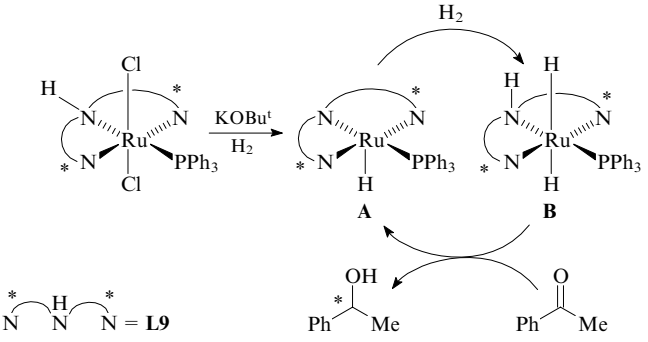
Many prochiral simple ketones may be hydrogenated with high enantioselectivity in the presence of Ru^{II}–ligand **L9** complex as a catalyst (Scheme 17).[15] The catalytic cycle proposed for this reaction is presented in Scheme 18.

Scheme 17



solv	*ee* (*R*) (%)	solv	*ee* (*R*) (%)
PhMe	59	MeOH	92
THF	67	EtOH	95
CH_2Cl_2	95	PriOH	94

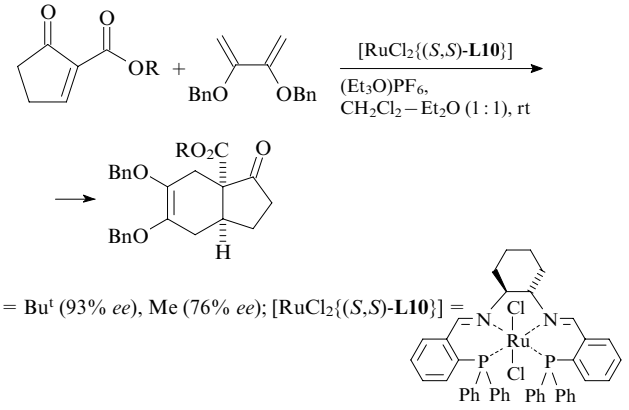
Scheme 18



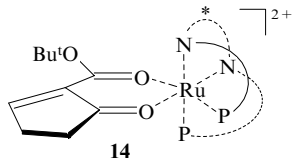
It has been assumed[15] that the hydride (Ru–H) and proton (N–H) moieties of the catalytic complex form a six-membered pericyclic transition state with the reacting carbonyl group similarly to bifunctional Noyori's catalyst.[16] The Ru···O coordination bond (with the carbonyl oxygen atom) in this transtition state has been later found experimentally.[17] As it may be seen from Scheme 18, the C_2 symmetry of the starting complex is lost upon the formation of intermediates **A** and **B**, which control the asymmetric induction. It is realized in two steps, thus being an example of stepwise mechanism. However, the proposed mechanism does not explain the pronounced influence of the solvent on the enantioselectivity of the reaction under consideration.

The reaction of ketoesters with butadiene derivative is catalyzed by C_2-symmetric [$RuCl_2${(*S*,*S*)-**L10**}] (Scheme 19).[18]

Scheme 19



On the basis of X-ray diffraction data, it was demonstrated that the ketoester was coordinated to the metal with the formation of asymmetric (*cis*-α) structure **14**.[18]

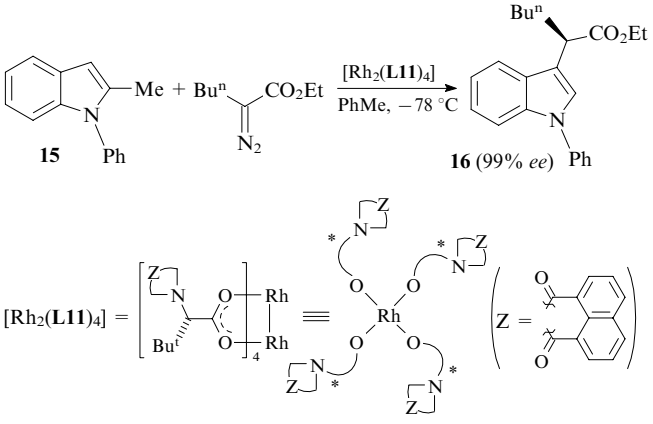


14

Presumsably, the first and, probably, the key intermediate of this reaction has a similar structure. As it follows from the experiment, replacement of the methyl group by a *tert*-butyl group leads to a dramatic increase in the enantioselectivity. This corresponds to the supposed structure of the key intermediate similar to structure **14**. Indeed, the lower the symmetry of the catalyst or the key intermediate, the higher the enantioselectivity of the reaction.[1,2] Therefore, the enantioselectivity of the diene attack at the second step of the reaction (stepwise mechanism of asymmetric induction) should be higher if R = Bu^t than in the case of R = Me, because in the former case, the symmetry of intermediate is lower.

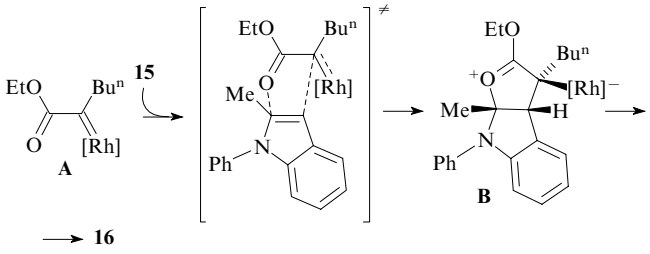
The C–H functionalization of indoles (*e.g.*, compound **15**) by diazo compounds (Scheme 20) is catalyzed by D_2-symmetric chiral binuclear rhodium complex $[Rh_2(\mathbf{L11})_4]$.[19] Its structure is confirmed by X-ray diffraction data.

Scheme 20



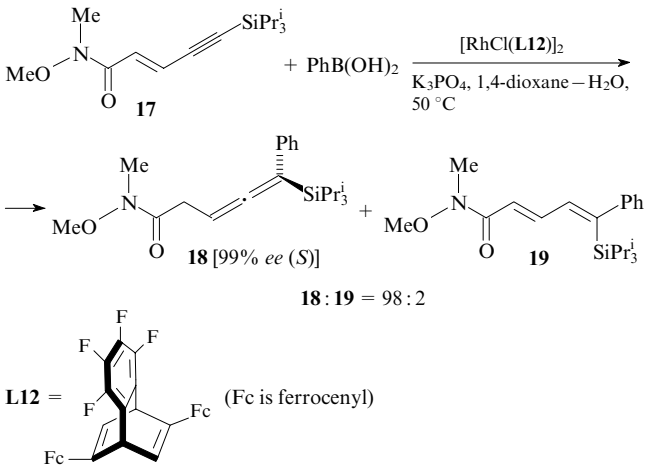
Taking into consideration the results of DFT calculations, a mechanism of this reaction resulting in product **16** was proposed (Scheme 21). As can be seen from Scheme 21, the D_2 symmetry of the rhodium complex $[Rh_2(\mathbf{L11})_4]$ = [Rh] is lost at intermediate **A**. According to this mechanism, the asymmetric induction proceeds in two steps *via* intermediates **A** and **B**.

Scheme 21



The enantioselective 1,6-addition of arylboronic acids to enynamides (*e.g.*, the addition of phenylboronic acid to compound **17** with the formation of chiral allenylsilane **18**) is catalyzed by rhodium complex with C_2-symmetric chiral diene ligand **L12** (Scheme 22).[20]

Scheme 22

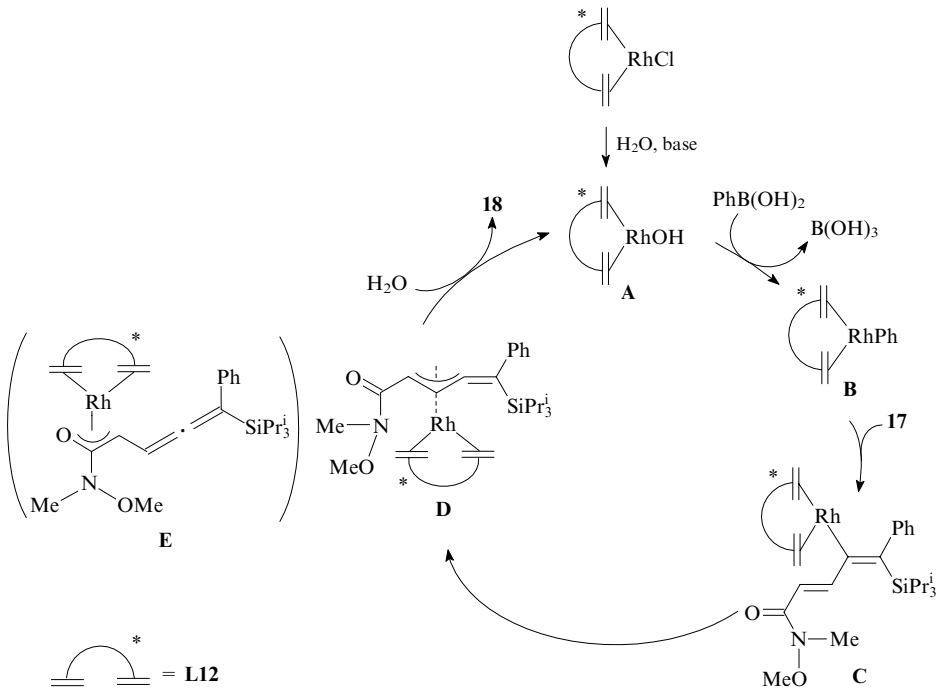


Along with allenylsilane **18**, the reaction gives diene **19** in small quantities. A possible mechanism of this reaction is shown in Scheme 23.

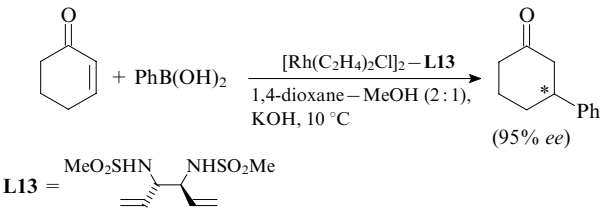
The phenyl group exchange between the boron and rhodium atoms with the subsequent introduction of alkyne at the Rh–Ph bond furnishes alkenyl rhodium intermediate **C** formed from C_2-symmetric intermediate **A** *via* complex **B**. This asymmetric chiral intermediate may be the key intermediate that determines the asymmetric induction. It isomerizes to benzylidene-π-allylrhodium **D**. Hydrolysis of this complex or of oxa-π-allylrhodium **E** results in product **18** and regeneration of C_2-symmetric intermediate **A**. Thus, asymmetric induction occurs in two (or three) steps, *i.e.*, the stepwise mechanism is realized.

A similar mechanism of asymmetric induction is possible in the conjugate addition of phenylboronic acid to α,β-unsaturated carbonyl compounds under the action of rhodium complex with chiral C_2-symmetric diene ligand **L13** (Scheme 24).[21]

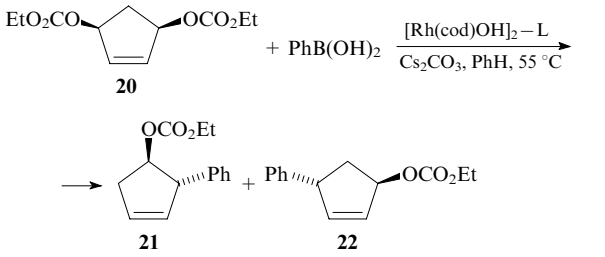
Scheme 23



Scheme 24

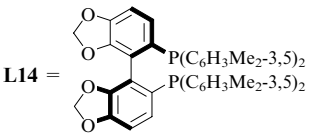


Scheme 25



A similar addition reaction of phenylboronic acid catalyzed by rhodium complexes with C_2-symmetric chiral diphosphines **L7** and **L14** may lead to desymmetrization of *meso*-3,5-di(ethoxycarbonyloxy)cyclopentene (**20**) (Scheme 25).[22] Chiral regioisomeric monoesters **21** and **22** are formed with high enantioselectivity.

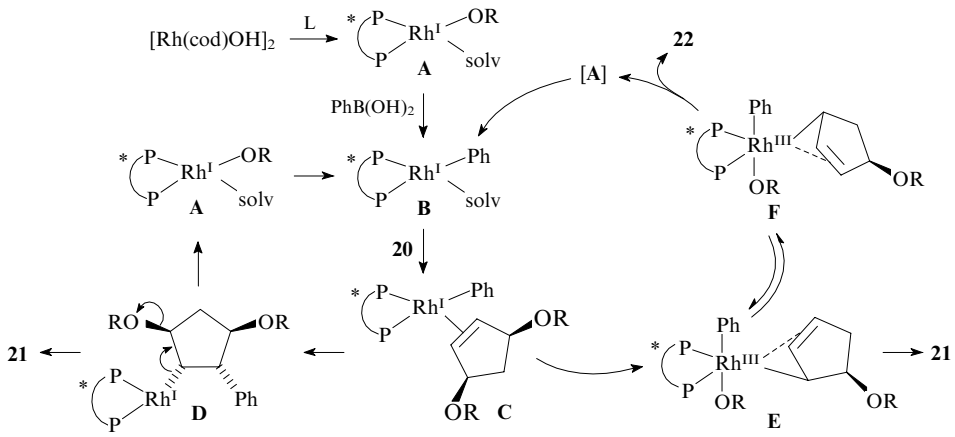
cod is cycloocta-1,5-diene,



L	**21** : **22**	*ee* (%)	
		21	**22**
L7	1 : 2.5	94	> 99
L14	1 : 2	97	99

Menard *et al.*[22] proposed a detailed mechanism of these reactions (Scheme 26). The reaction of asymmetric complex **A** with phenylboronic acid leads to phenyl group exchange between the B and Rh atoms with the formation of intermediate **B**. In the authors' opinion, after coordination of the substrate in intermediate **C**, there may be two possible reaction routes, one giving product **21** *via* intermediate **D** and the other giving products **21** and **22** *via*

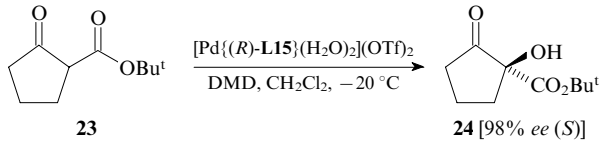
Scheme 26



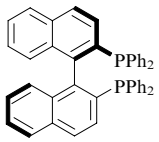
intermediates **E** and **F**. In both cases, the asymmetric induction is realized *via* stepwise mechanism.

The α-hydroxylation of 1,3-ketoesters is also catalyzed by Pd complex with (*R*)-BINAP [(*R*)-**L15**] with high enantioselectivity (Scheme 27).[23] For example, using ketoester **23** as the starting compound, it is possible to obtain tertiary alcohol **24**.

Scheme 27

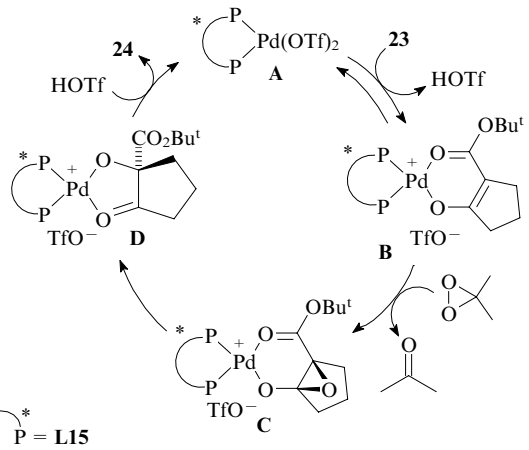


23 **24** [98% *ee* (*S*)]

(*R*)-**L15** =  , DMD is dimethyldioxirane

A possible catalytic cycle of this reaction is presented in Scheme 28. It is supposed[23] that **D** → **A** is the rate-determining step. However, the asymmetric carbon atom is formed in intermediate **D**. Therefore, the asymmetric induction of this reaction, according to the proposed mechanism, proceeds *via* consecutive steps involving asymmetric intermediates **B** → **C** and **D** (stepwise mechanism).

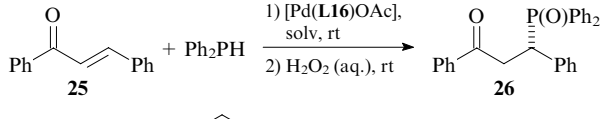
Scheme 28



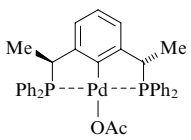
P P = **L15**

The addition reaction of diarylphosphines to enones (*e.g.*, compound **25**) proceeds with high enantioselectivity under the action of C_2-symmetric palladium complex with pincer type ligand **L16** (Scheme 29).[24]

Scheme 29



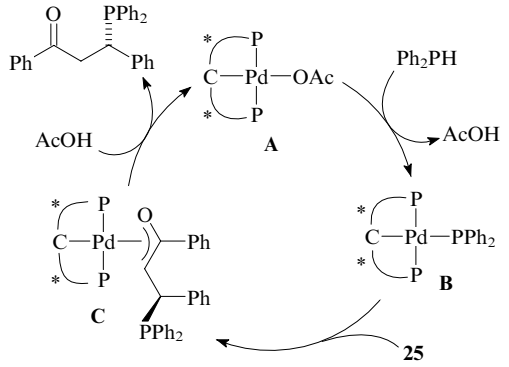
25 **26**

[Pd(**L16**)OAc] = 

solv	*ee* (%)
CH_2Cl_2	99
PhMe	98
THF	99
Bu^{t}OH	99
MeCN	99

As can be seen from the catalytic cycle given in Scheme 30, the asymmetric induction goes in two steps *via* intermediate **B** and asymmetric intermediate **C**, which is converted to chiral phosphine (the precursor of phosphine oxide **26**).

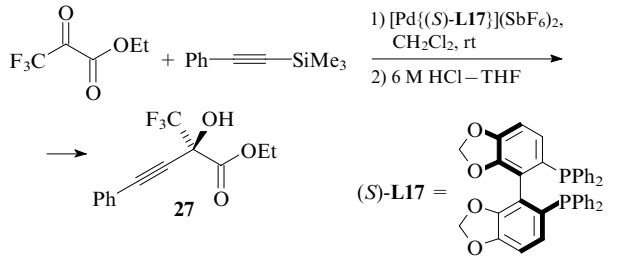
Scheme 30



P C P = **L16**

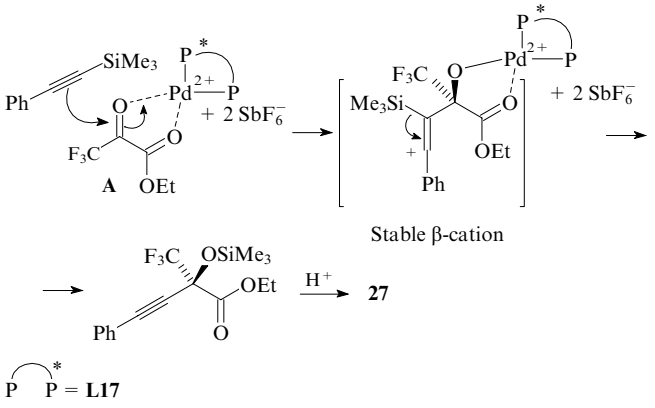
The C_2-symmetric palladium complex with ligand **L17** possessing axial chirality catalyzes alkynylation of trifluoropyruvate by alkynylsilane with the formation of tretiary alcohol **27** (Scheme 31).[25]

Scheme 31



According to the possible mechanism of this reaction (Scheme 32), asymmetric induction is realized in two consecutive steps *via* asymmetric intermediate **A**. A similar mechanism has also been proposed for reactions of similar substrates in the presence of (*S*)-**L15** – Pd complex as a catalyst (99% *ee*).[26]

Scheme 32

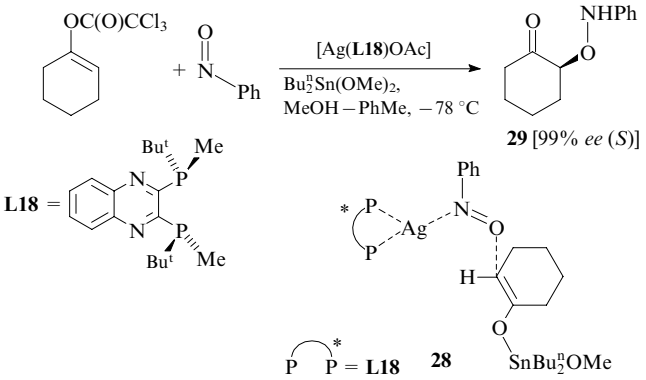


P P = **L17**

The aldol reaction taking place between nitrosobenzene and alkenyl trichloroacetate in the presence of

$Bu^n_2Sn(OMe)_2$ is catalyzed by the silver complex with C_2-symmetric diphosphine ligand **L18** (Scheme 33).[27] Yanagisawa *et al.*[27] proposed a possible structure of intermediate **28**, leading to product **29**. In the first step, the silver atom of the complex catalyst coordinates the nitrogen atom of nitrosobenzene, the C_2 symmetry of the starting complex being lost. The tin enolate complex formed as a result of reaction of alkenyl trichloroacetate with $Bu^n_2Sn(OMe)_2$ reacts with nitrosobenzene to give product **29** with regeneration of $Bu^n_2Sn(OMe)_2$ and the starting complex catalyst. Thus, in the reaction under consideration, asymmetric induction occurs in two consecutive steps.

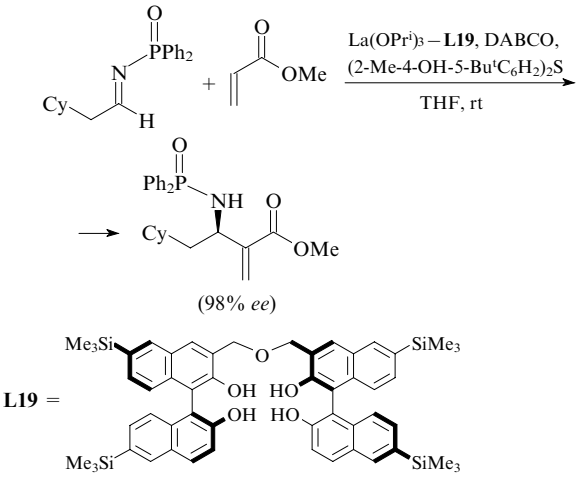
Scheme 33



The combined use of complex [La(**L19**)] † and 1,4-diazabicyclo[2.2.2]octane (DABCO) promotes aza-version of the Morita – Baylis – Hillman reaction of electron-deficient alkenes with imines in the presence of diphenyl sulfide (Scheme 34).[28]

† From here on, for the sake of simplicity, we will designate both free and coordinated ligands by the same number even if the ligand loses protons upon coordination, as in the case of ligand **L19**.

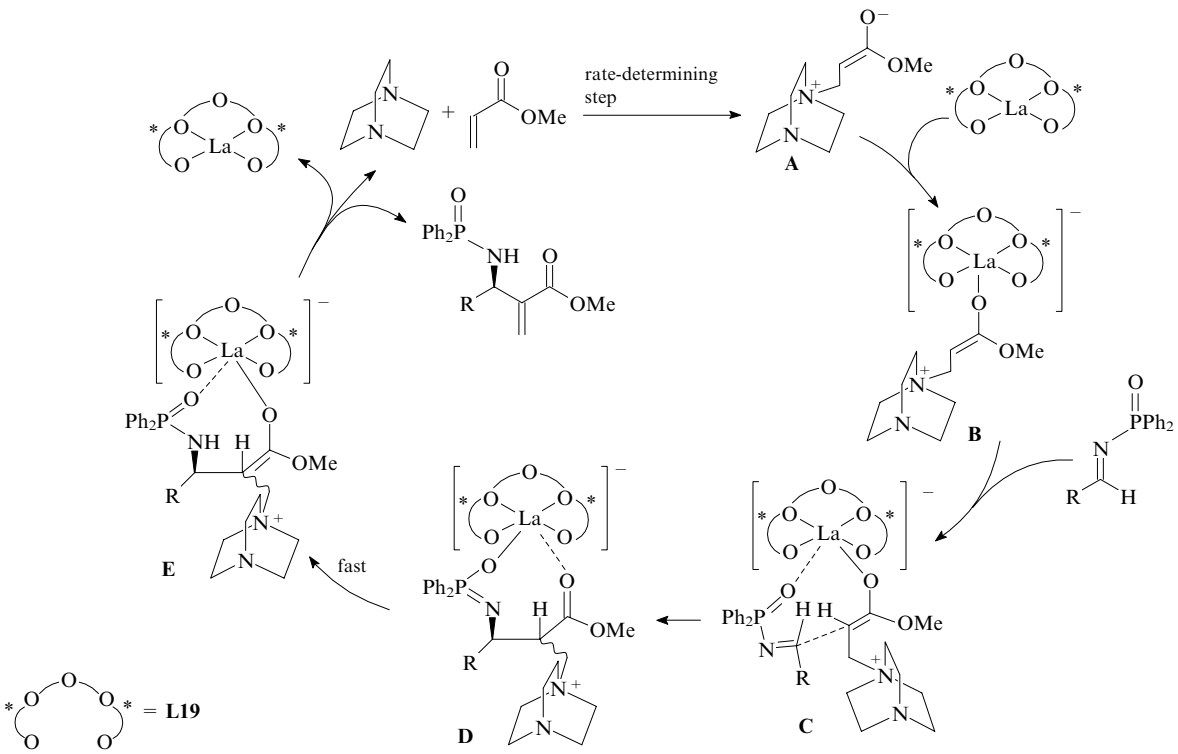
Scheme 34



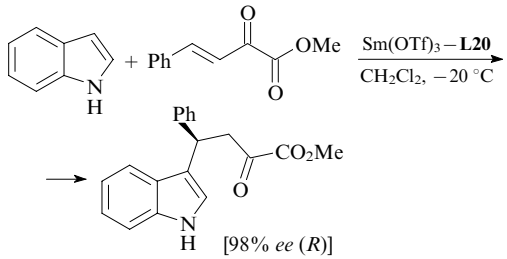
A proposed [28] catalytic cycle based on the kinetic studies is shown in Scheme 35. Complex [La(**L19**)] reacts with zwitter-ion **A** with the formation of asymmetric key intermediate **B**. After coordination of iminophosphine oxide to the La atom (as the Lewis acid) of intermediate **C**, the catalytic cycle proceeds *via* intermediates **D** and **E** possessing an asymmetric carbon atom. Intermediate **E** dissociates into the reaction product and the starting diamine (DABCO) and lanthanum complex. The successive steps **B(C)** → **D(E)** provide asymmetric induction *via* stepwise mechanism.

The Friedel – Crafts reaction of indole with β,γ-unsaturated α-ketoesters is catalyzed by samarium complex with C_2-symmetric chiral ligand **L20** (Scheme 36).[29]

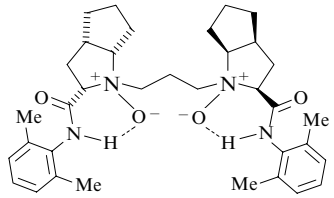
Scheme 35



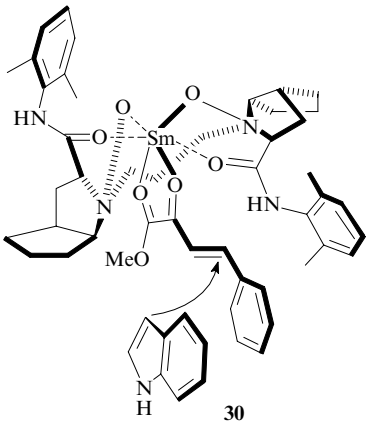
Scheme 36



L20 =



The structure of the possible key intermediate of this reaction has been proposed [29] (structure **30**).



30

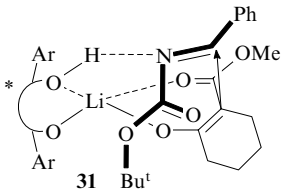
Obviously, the intermediate that has lost its C_2 symmetry is attacked by indole. The reaction proceeds in two successive steps.

It is necessary to emphasize that the proposed differentiation of the reactions described in this and next chapters according to the mechanism of asymmetric induction has a probabilistic character. It is based on the proposed catalytic cycles, which have been more or less proved by the authors of the cited papers. However, the conclusions about the asymmetry of the intermediates that control the asymmetric induction are more reliable, as they are based on stereochemical logic and have been partially proved by experiments or calculations (see, *e.g.*, Ref. 30).

2. Cooperative mechanism of asymmetric induction

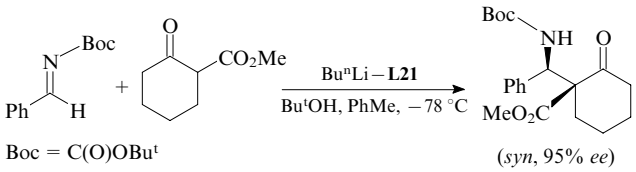
The asymmetric Mannich-type reaction of aldimines with cyclic ketoesters is catalyzed by lithium salt of diol (*R*)-3,3′-(3,4,5-$F_3C_6H_2$)$_2$BINOL (**L21**) (Scheme 37).[31]

For this reaction, the authors [31] have proposed a transition state **31** in which both reactants are bound to catalytic complex.



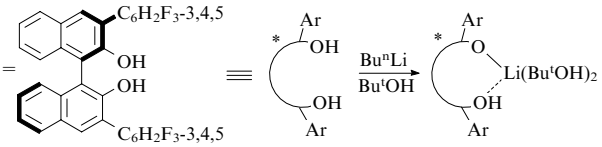
31

Scheme 37



Boc = C(O)OBu^t

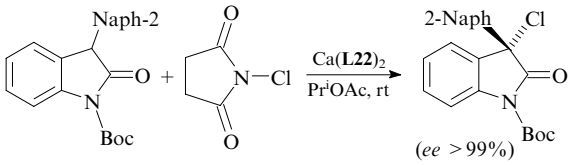
L21 =



Hence, the asymmetric induction is probably realized in one step according to the cooperative mechanism with C_1 symmetry of the key intermediate.

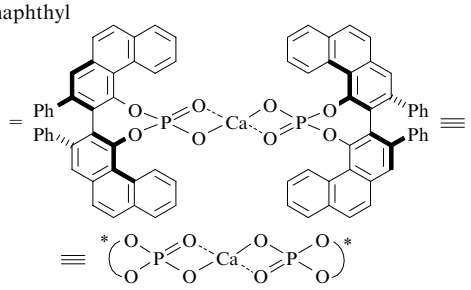
Chlorination of 3-substituted oxindoles with *N*-chlorosuccinimide in the presence of C_2-symmetric chiral calcium phosphate complex Ca(**L22**)$_2$ proceeds enantioselectively (Scheme 38).[32]

Scheme 38

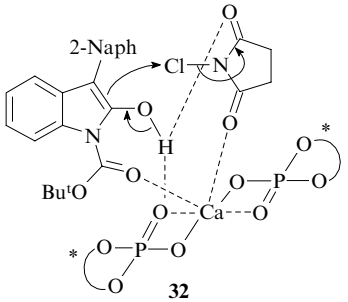


Naph is naphthyl

Ca(**L22**)$_2$ =



Zheng *et al.*[32] proposed the structure of possible intermediate **32** of this reaction. This structure was based on the bifunctional character of calcium complex, which activates both nucleophile and electrophile. The coordination of the Boc and succinimide oxygen atoms by Ca creates the reaction centre; the hydroxyl group of the oxindole tautomer may be hydrogen-bonded to the P=O group of the catalyst. Both reactants are bonded to the catalytic complex, which has lost C_2 symmetry, and asymmetric induction is likely realized in one step.

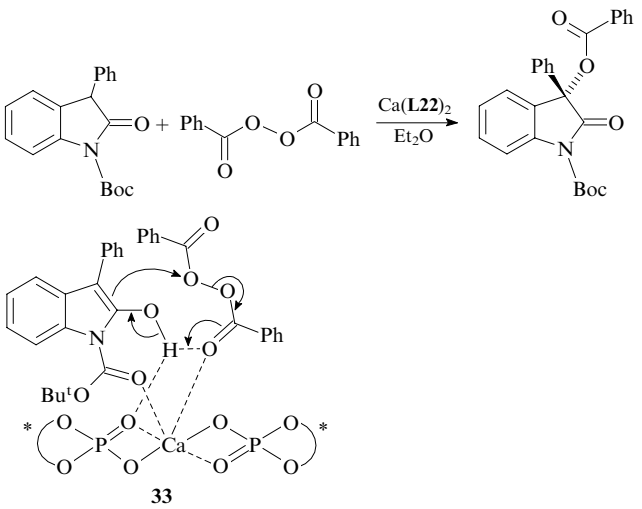


32

A similar structure of the transition state may also be present in the reaction of oxindoles with peroxides (Scheme 39).[33] The cooperative mechanism of asymmetric

induction with intermediate **33** is also most probable in this case.

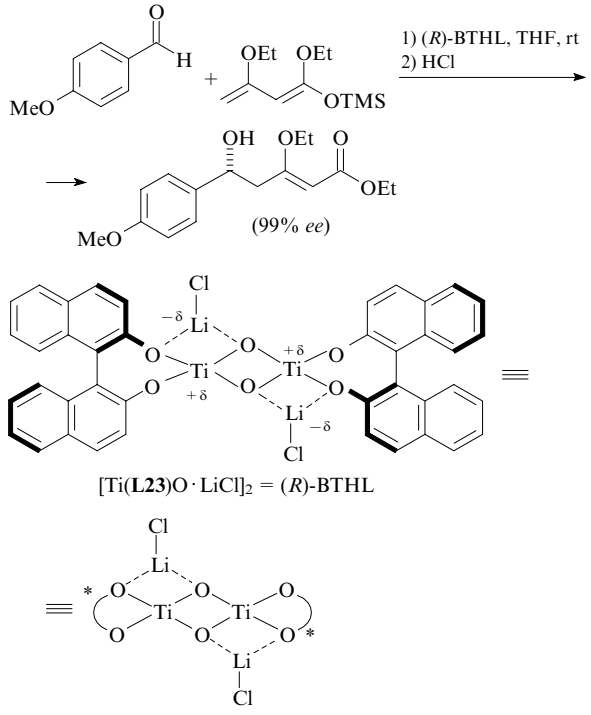
Scheme 39



33

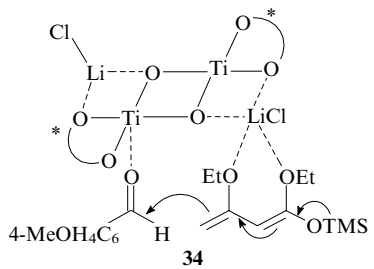
The catalytic system generated from (*R*)-BINOL (**L23**), $Ti(OPr^i)_4$, H_2O and LiCl catalyzes the aldol reaction of Brassard's diene and aromatic aldehydes (Scheme 40).[34]

Scheme 40



[Ti(**L23**)O · LiCl]$_2$ = (*R*)-BTHL

The authors have proposed the working model for the catalytic complex **34** (the transition state of this reaction) with a pronounced bifunctional character.



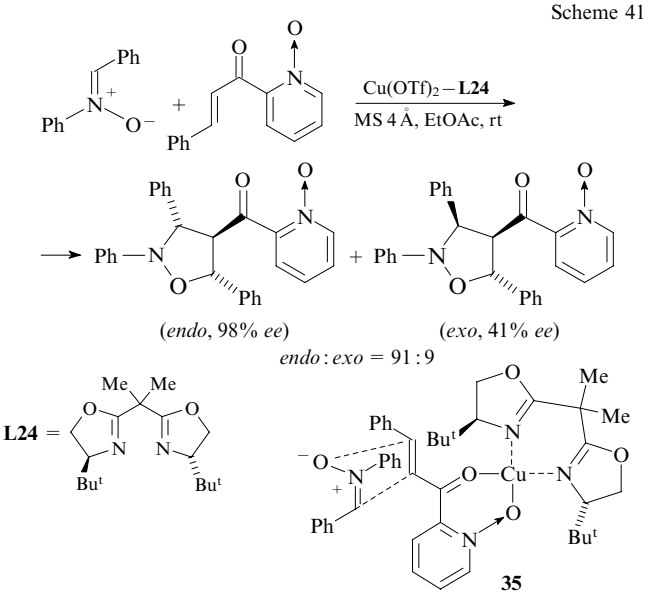
34

It can be seen that the product is formed as a result of interaction of aldehyde and diene coordinated by the Ti and Li atoms (the Lewis acids) of BTHL. The reactant coordination eliminates the C_2 symmetry of this complex. Thus, the cooperative mechanism of asymmetric induction involving asymmetric complex is quite realistic for this reaction.

It is possible to deduce the cooperative mechanism of asymmetric induction from the mechanism proposed [35] for the addition of nitroalkenes to substituted oxindoles in the presence of Ni complex with C_2-symmetric chiral diamine (97% *ee*).

The cycloaddition of nitrone to 2-alkenoylpyridine *N*-oxide is catalyzed by the copper complex with C_2-symmetric chiral ligand **L24** in the presence of molecular sieves (MS) (Scheme 41).[36]

Scheme 41



(*endo*, 98% *ee*) (*exo*, 41% *ee*)

endo : *exo* = 91 : 9

L24 =

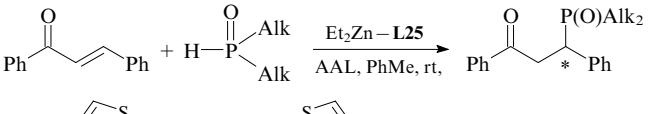
35

Barroso *et al.* [36] proposed a stereochemical model of key intermediate **35** for this reaction. This structure was asymmetric, the Cu coordination environment having an extended square-bipyramidal geometry with two axial triflate anions (the latter are omitted in structure **35** for clarity). Thus, the mechanism of asymmetric induction is cooperative.

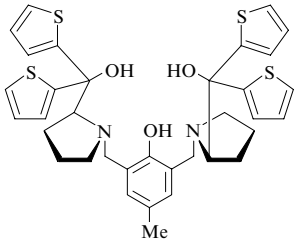
A similar structure was proposed for the intermediate of catalytic alkylation of indoles with nitroalkenes (the Friedel – Crafts reaction) under the action of $Cu(OTf)_2$ complex with C_2-symmetric chiral diamine containing two sulfonamide moieties (97% *ee*).[37] This suggests that in this reaction, the mechanism of asymmetric induction would also be cooperative.

The catalytic addition of dialkylphosphine oxides to α,β-unsaturated ketones proceeds in the presence of diethylzinc and C_2-symmetric ligand **L25** (Scheme 42).[38]

Scheme 42

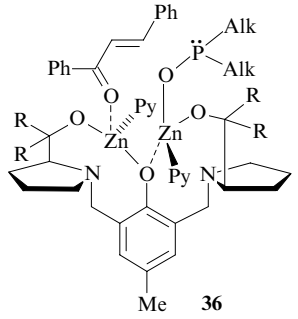


L25 =



AAL	*ee* (%)
Pyridine	99
–	93

Structure **36** has been proposed as a key intermediate of this reaction.

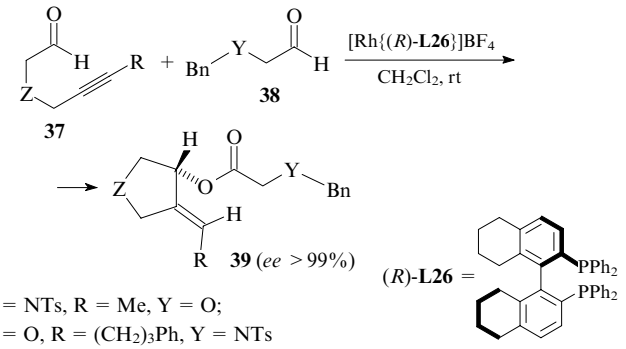


R is 2-thienyl, Py is pyridine

On these grounds, it is possible to draw the conclusion of cooperative mechanism of asymmetric induction. A similar zinc complex catalyzes the hydrophosphinylation of α,β-unsaturated *N*-acylpyrroles with dialkylphosphine oxides with *ee* > 99%.[39] In this reaction, which is similar to the reaction of Scheme 42, the cooperative mechanism of asymmetric induction is also quite probable.

Reductive cyclization of 3-aza- or 3-oxaalk-5-ynals **37** with substituted acetaldehydes **38** is catalyzed by the Rh complex with (*R*)-(H_8-BINAP) ligand (**L26**) (Scheme 43).[40]

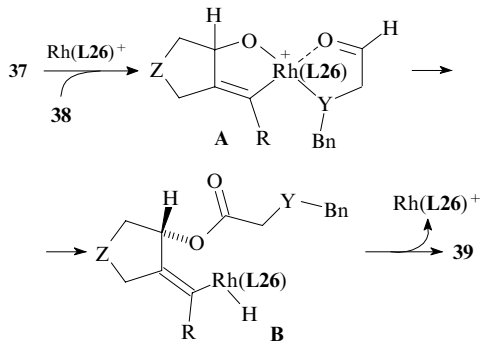
Scheme 43



Z = NTs, R = Me, Y = O;
Z = O, R = $(CH_2)_3$Ph, Y = NTs

A possible reaction mechanism is given in Scheme 44. The authors[40] assume that alkynal **37** and acetaldehyde **38** are coordinated by the rhodium complex to form asymmetric intermediate **A**. The interaction of the aldehyde group with the Rh—O moiety leads to intermediate **B** containing coordinated chiral product **39**. Since according to this scheme, the key intermediate **A** is formed in one step, the mechanism of asymmetric induction is cooperative.

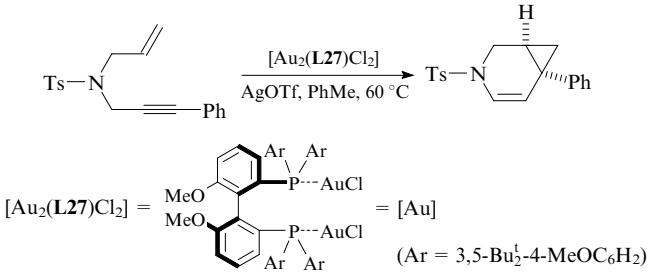
Scheme 44



Cooperative mechanism of asymmetric induction is also most possible for the addition of substituted trifluoroborates to *N*-sulfonyl ketimines catalyzed by the rhodium complex with C_2-symmetric chiral diene (98% – 99.5% *ee*).[41]

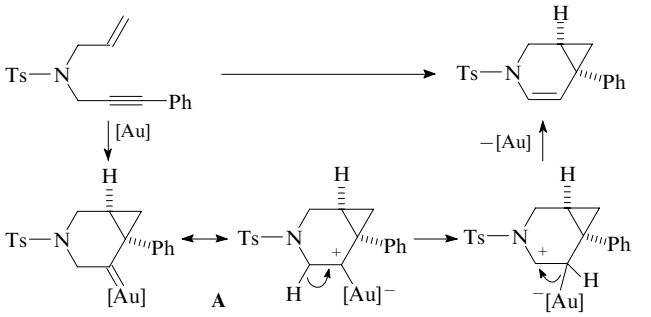
The cycloisomerization of 4-aza-1,6-enynes to azabicyclo[4.1.0]heptenes is catalyzed by binuclear Au(I) complex with ligand **L27** (Scheme 45).[42]

Scheme 45



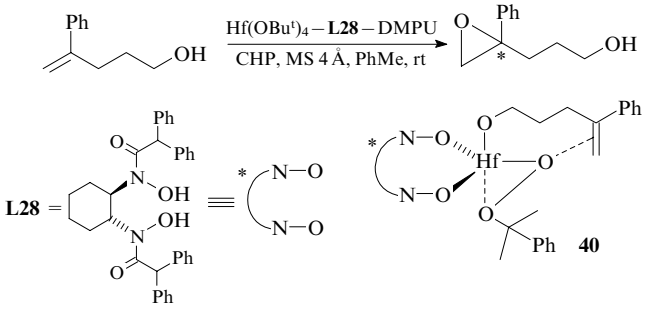
According to the mechanism proposed[42] for this reaction, the asymmetric induction is realized in one step (cooperative mechanism) *via* asymmetric intermediate **A** (Scheme 46).

Scheme 46



Cooperative mechanism of asymmetric induction is also possible in the epoxidation of homo- and bishomoallylic alcohols (Scheme 47) catalyzed by hafnium complex with C_2-symmetric ligand **L28**.[43]

Scheme 47



DMPU is 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1H)-one, CHP is cumene hydroperoxide

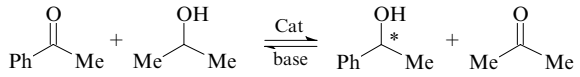
A possible structure **40** of the intermediate complex responsible for asymmetric induction was proposed.[43] According to this structure, the product may form in one step, *i.e.*, by cooperative mechanism. Unfortunately, this scheme does not disclose the functions of the achiral additional reagent (ligand), DMPU, and of molecular sieves.

As it was already mentioned, classification of the asymmetric induction types into two- or one-step one (*i.e.*, stepwise or cooperative mechanism, respectively) was not proved experimentally in most cases and is based only on the possible mechanisms proposed by the authors of the cited papers. However, considering all of the mechanisms discussed, it is possible to assume that the key intermediates responsible for the asymmetric induction in highly enantioselective reactions (listed above) catalyzed by C_2-symmetric complexes are asymmetric.

III. C_2-Symmetric intermediates controlling asymmetric induction in the reactions involving complexes with C_2-symmetric chiral ligands

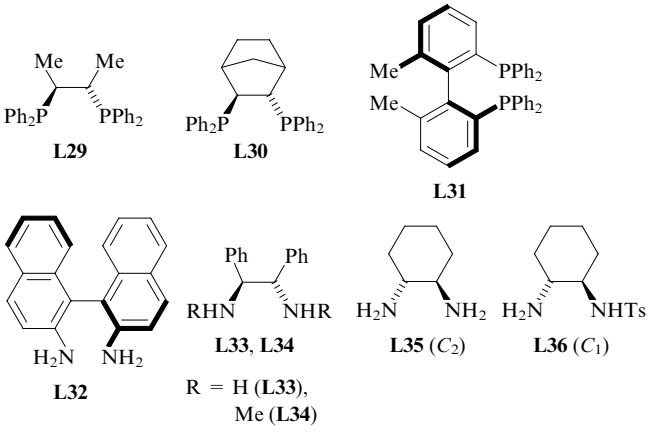
The enantioselectivities of the reactions of monofunctional substrates under the action of C_2- and C_1-symmetric complexes are significantly different.[1,2] Hydrogenation of prochiral ketones with hydrogen atom transfer is one of the most well-investigated asymmetric reactions catalyzed by chiral metal complexes (Scheme 48).[44]

Scheme 48



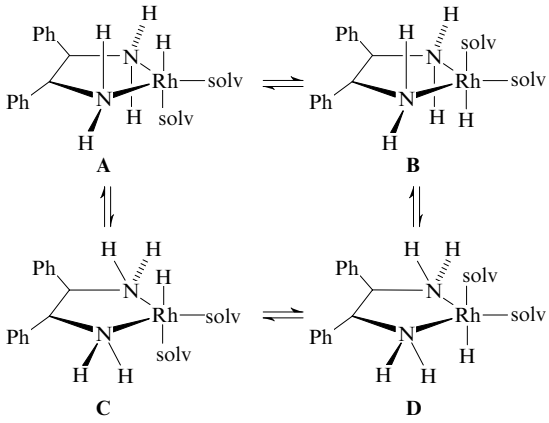
Ligand	Metal	*ee* (%)	Configuration of the product	Ref.
L2	Ru	1–4	*S*	45, 46
L29	Rh	< 1		47
	Ir	4–28	*S*	48
L30	Ru	28	*R*	49
L31	Ru	15	*R*	49
L32	Rh	0		50
L33	Rh	17	*R*	47, 48
L34	Rh	67	*R*	47, 48
L35	Rh	12	*S*	50
L36	Rh	97	*R*	51
	Ir	96	*R*	51

The very low *ee* values of the products of this reaction induced by Rh, Ir and Ru complexes with C_2-symmetric ligands **L2**, **L29**–**L35** attract special attention.[1–3,45,46]



The optical purity of the reaction products significantly increases on going to catalytic complexes with asymmetric ligands, as can be seen, for example, by comparing the data for Rh complexes with ligands **L35** and **L36**. For the complex Rh(**L33**), an equilibrium of chelate intermediates **A**, **B**, **C** and **D** is established in solution (Scheme 49).

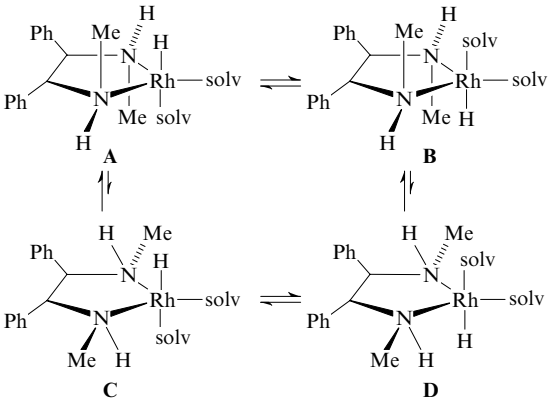
Scheme 49



If the equilibrium between complexes **A** and **B** is established rather quickly, both structures are C_2-symmetric and actually equivalent as catalytic complexes. As is generally known, for the reaction under consideration (see Scheme 48) involving rhodium complexes with diphosphine and diamine ligands, the step of asymmetric induction includes simultaneous transfer of the apical hydrogen H atom of the *trans*-RuH(Cl)(diphosphine)(diamine) intermediate and of the proton of the ligand RNH group to the carbonyl moiety of the substrate *via* a six-membered transition state.[52–54] If this concept is applied to rhodium–chiral N,N-ligand complexes, a six-membered transition state may be formed with participation of the pseudo-axial N–H bond and apical Rh–H bond of intermediate **A** and the enantiomeric NH–RhH moiety of intermediate **B** to give one and the same enantiomer of the product. The other enantiomer may be formed from the corresponding moieties of intermediates **C** and **D**. Taking into consideration the equilibria between intermediates (**A**, **B**, **C** and **D**), it is possible to assume that this reaction in the presence of complex Rh(**L33**) would have low enantioselectivity, and this corresponds to experimental data.

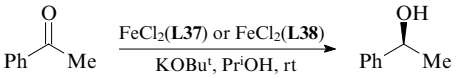
The complex rhodium–ligand **L34** has a stable chelate structure with stereogenic nitrogen atoms, as shown by DFT calculations[55] (intermediates **A** and **B**, Scheme 50). According to these calculations and analysis of molecular models, structures **A** and **B** are more preferable than **C** and **D**. That is why equilibrium is possibly shifted to intermediates **A** and **B**, from which one enantiomer of the product is formed. In this case, the reaction should proceed with slightly higher enantioselectivity than under the action of complex Rh(**L33**), which corresponds to the experimental data. In both cases (see Schemes 49 and 50), key intermediates **A** and **B** responsible for asymmetric induction have C_2 symmetry. This corresponds to comparatively low enantioselectivity (67% ee_{max}). For asymmetric ligand **L36** with substituents at the nitrogen atom greatly differing in volume, it is most probable that equilibrium is shifted to one out of the four possible intermediates. Then one may expect a large *ee* value of the product, which corresponds to the experimental data.

Scheme 50

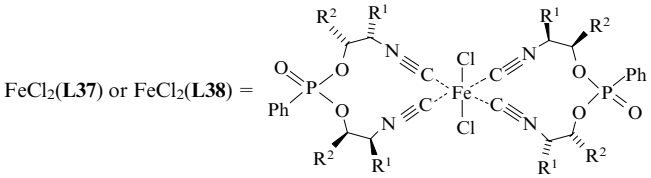


The considered reaction is also catalyzed by D_2-symmetric chiral iron complex with isonitrile ligand **L37** or **L38** (Scheme 51).[56]

Scheme 51



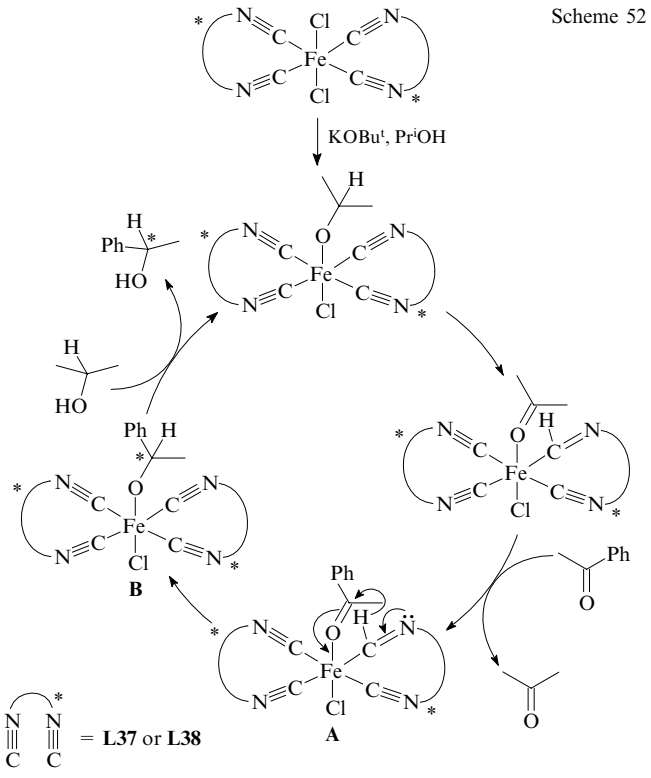
(64% *ee* for **L37**, 10% *ee* for **L38**)



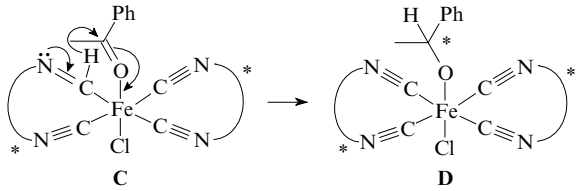
R^1 = Bu^t, R^2 = H (**L37**); R^1 = Pr^i, R^2 = Me (**L38**)

It is assumed[56] that the ketone carbonyl group is coordinated by the iron atom of the complex acting as a Lewis acid with the formation of intermediates **A** and **B** (Scheme 52). The reduced isonitrile group acts as the hydride donor. Intermediates **C** and **D** (Scheme 53), being alternative to intermediates **A** and **B** of this reaction, lead to products with the opposite configuration. That is why the enantioselectivity of this reaction should not be high, which corresponds to the experiment. It should be noted that the mechanism under discussion does not hold for substrates capable of two-point coordination. As an illustration, compare the reactions of two substrates given in Scheme 54.[56]

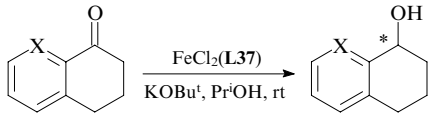
Scheme 52



Scheme 53



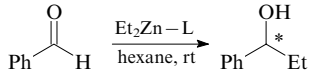
Scheme 54



[91% *ee* (X = N), 46% *ee* (X = CH)]

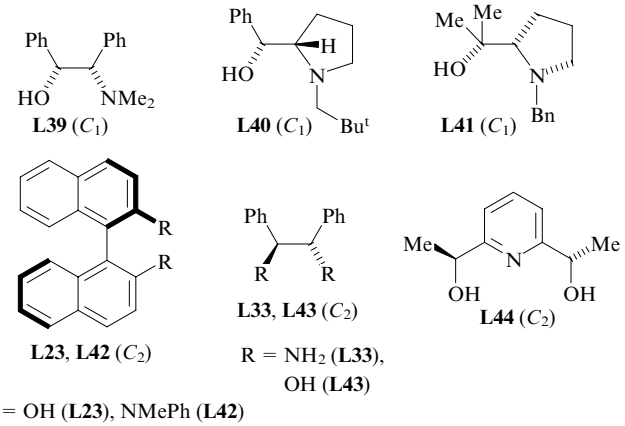
The addition of dialkylzinc to benzaldehyde is another well-studied reaction with an extremely big difference in the enantioselectivities depending on the symmetry (C_2 or C_1) of chiral complex catalysts. It is the first step of the reaction shown in Scheme 55.[1]

Scheme 55



L	*ee* (%)	Configuration of the product	Ref.	L	*ee* (%)	Configuration of the product	Ref.
L39	97	*R*	57	**L33**	26	*S*	60
L40	100	*R*	58	**L42**	8	*R*	61
L41	99	*R*	59	**L43**	20	*R*	60
L23	8	*S*	60	**L44**	4	*S*	62

The catalytic cycle of this reaction was proposed for asymmetric ligands of **L39**–**L41** types based on calorimetric kinetic measurements.[63]

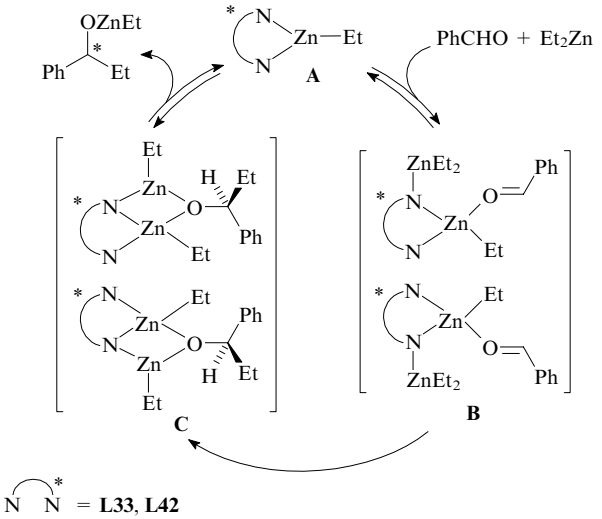


R = OH (**L23**), NMePh (**L42**)

The decrease in the enantioselectivity on going from these asymmetric ligands to C_2-symmetric ligands **L33**, **L42**

may be explained using a similar catalytic cycle (Scheme 56).

Scheme 56

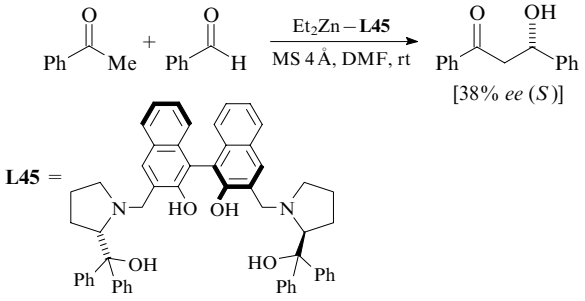


N N* = **L33**, **L42**

In this Scheme, the key intermediate **A** is C_2-symmetric. Two possible structures of intermediate **B** are mirror images. Thus, according to this Scheme, it is possible to expect the formation of racemic product or the product with a low optical purity. This is actually observed in the experiment with C_2-symmetric ligands **L23**, **L33**, **L42**, **L43** and **L44**.

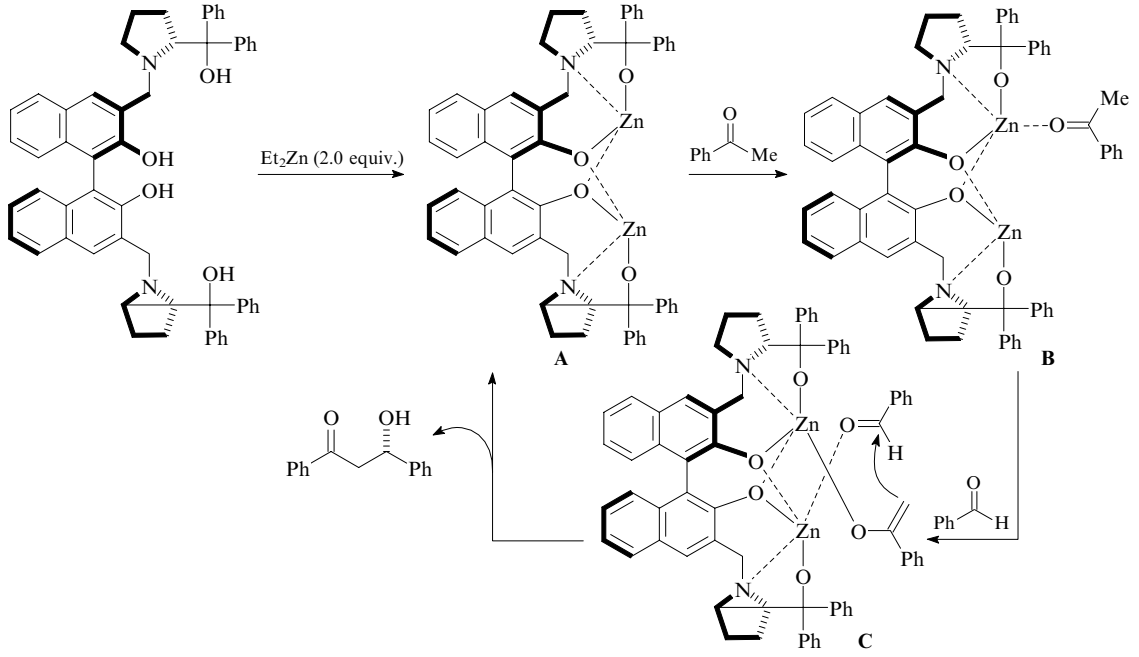
This mechanism also accounts for the relatively low enantiomeric purity of the product of aldol reaction of aryl ketones with arylaldehydes (Scheme 57) in the presence of zinc complex with C_2-symmetric ligand **L45**.[64]

Scheme 57

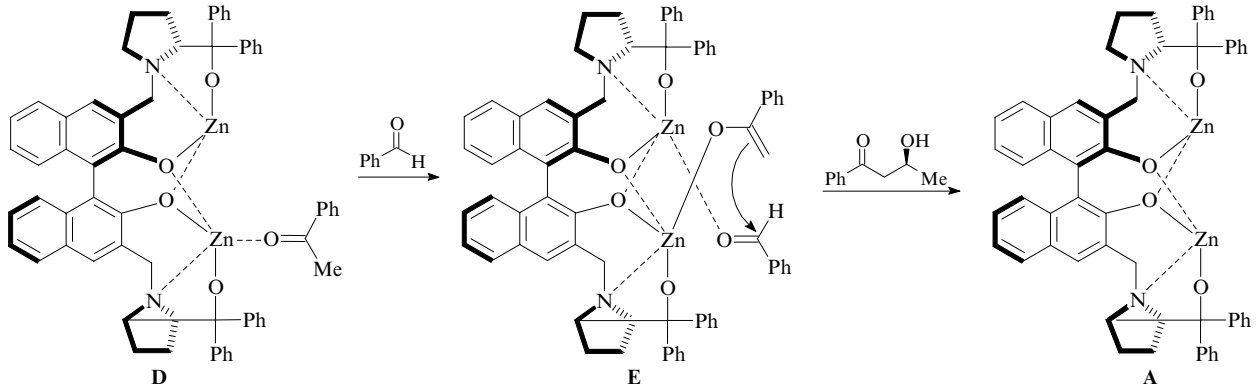


The sequence of intermediates given in Scheme 58 has been proposed for this reaction.[64] Apparently, key intermediate **A** responsible for asymmetric induction has C_2 symmetry. An alternative pathway of this reaction is possible, namely, that *via* intermediate **D** (Scheme 59), which is the mirror image of intermediate **B**. This pathway leads to

Scheme 58



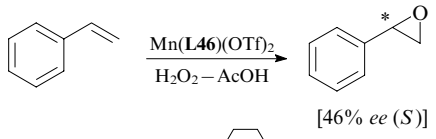
Scheme 59

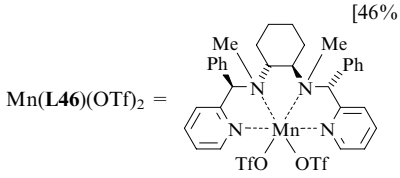


enantiomeric product *via* intermediate **E**. It explains the low enantioselectivity of the reaction.

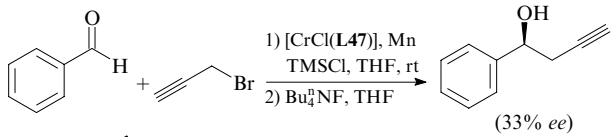
A similar explanation of low enantioselectivity is possible for epoxidation of alkenes catalyzed by manganese complex with C_2-symmetric ligand **L46** (Scheme 60)[65] and for propargylation of aldehydes under the action of chromium complex with C_2-symmetric ligand **L47** (Scheme 61).[66]

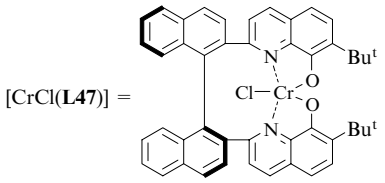
Scheme 60





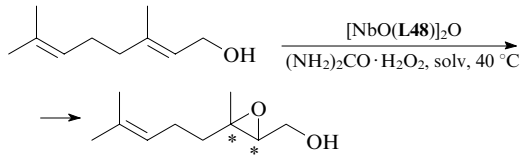
Scheme 61

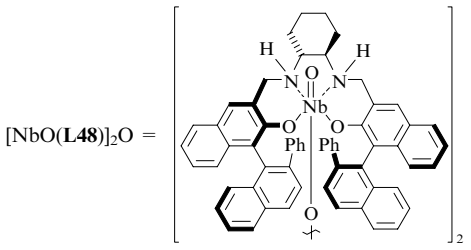




The enantioselectivity of epoxidation of allylic alcohols catalyzed by C_2-symmetric niobium salan complex $[NbO(\mathbf{L48})]_2O$ strongly depends on the solvent (Scheme 62).[67]

Scheme 62



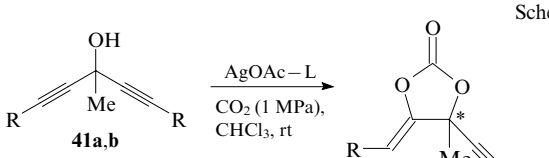


solv	*ee* (%)
PhMe	81
EtOAc	56
MeOH	0

The formation of racemic product in methanol is probably caused by substitution of the solvent for the diene OH group coordinated to chiral complex (this coordination starts the enantioselective reaction).

A C_2-symmetric key intermediate is also possible in the desymmetrization of bispropargylic alcohols **41a**,**b** upon the reaction with carbon dioxide under the action of C_2-symmetric silver complexes with ligands **L49** and **L50** (Scheme 63).[68]

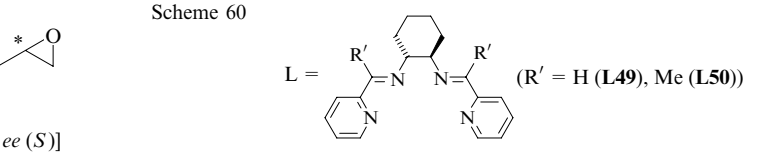
Scheme 63



41a,**b**

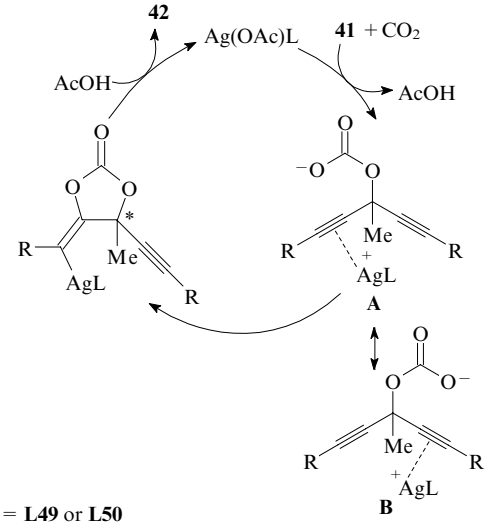
For **41a**: R = Ph, L = **L49**;
for **41b**: R = CH_2OBn, L = **L50**

42a,**b** (40% *ee*)



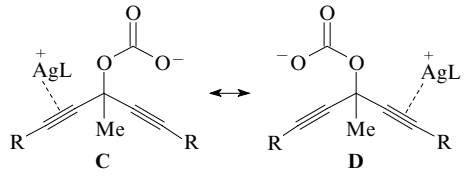
As in the reaction presented in Scheme 57, intermediates **A** and **B** (Scheme 64), and also alternative intermediates **C** and **D** (Scheme 65) are both possible. They lead to different enantiomers of products **42a**,**b**. The low enantioselectivity of the reaction under consideration is explained by this fact.

Scheme 64



L = **L49** or **L50**

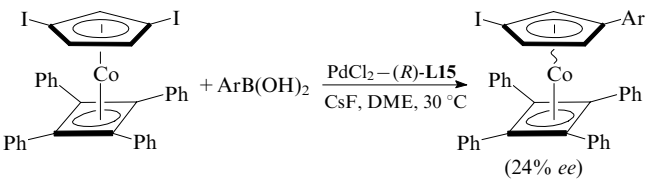
Scheme 65



L = **L49** or **L50**

A similar explanation of low enantioselecivity may apply desymmetrization of cobalt-bis(cyclodiene) complexes in the reaction with arylboronic acid (Scheme 66).[69]

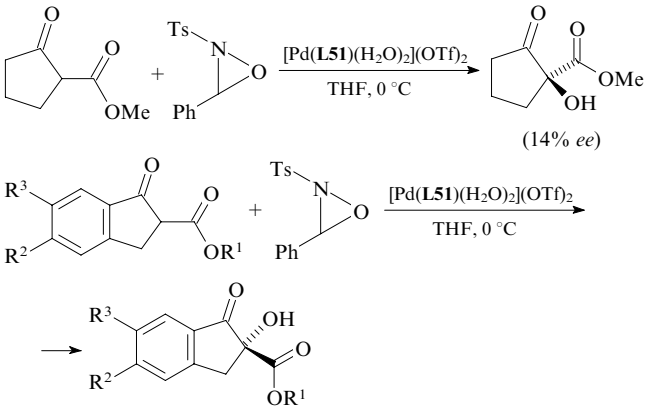
Scheme 66



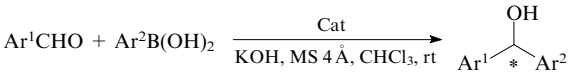
Ar = 2-$MeOC_6H_4$

Low enantioselectivity of a series of reactions catalyzed by palladium complexes with atropoisomeric ligands **L51** and **L52** (Scheme 67) is also attributable to the C_2 symmetry of the key intermediate determining the asymmetric induction.[70, 71]

Scheme 67



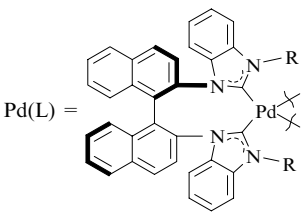
R^1	R^2	R^3	*ee* (*R*) (%)	R^1	R^2	R^3	*ee* (*R*) (%)
Me	H	H	61	Me	Cl	H	61
Pr^i	H	H	37	Et	Cl	H	51
Bu^t	H	H	18	Me	H	Br	42
Bn	H	H	30	Et	H	Br	51



cat = [Pd(**L52**)$(H_2O)_2$](OTf)$_2$ + [Pd(**L52**)$(OC(O)CF_3)_2$] (1 : 1)

Ar^1	Ar^2	*ee* (%)[a]	Ar^1	Ar^2	*ee* (%)[a]
4-$O_2NC_6H_4$	2-MeC_6H_4	10 (*S*)	2-ClC_6H_4	4-PhC_6H_4	13 (*S*)
4-$O_2NC_6H_4$	3-MeC_6H_4	21 (+)	2-ClC_6H_4	Ph	13 (*S*)
4-$O_2NC_6H_4$	4-MeC_6H_4	48 (+)	2,4-$Cl_2C_6H_3$	Ph	65 (*S*)
4-$O_2NC_6H_4$	2-Naph	20 (−)	2-$O_2NC_6H_4$	4-PhC_6H_4	5 (+)
3-$O_2NC_6H_4$	2-Naph	29 (+)	2,4-$Cl_2C_6H_3$	3-MeC_6H_4	50 (+)
3-$O_2NC_6H_4$	4-PhC_6H_4	1 (−)	2,4-$Cl_2C_6H_3$	3-MeC_6H_4	40 (+)
4-$MeOC_6H_4$	4-PhC_6H_4	6 (+)	2,4-$Cl_2C_6H_3$	4-MeC_6H_4	40 (+)

[a] Product configuration or sign of rotation is given in parentheses.

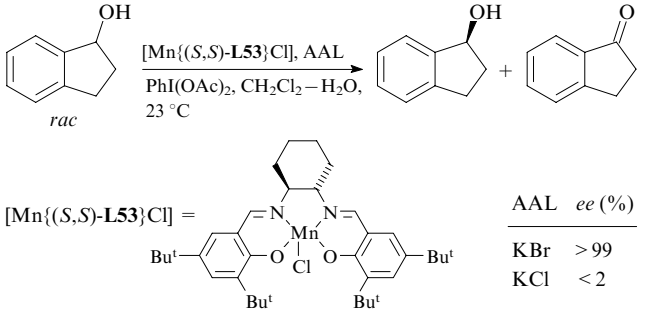


[L = **L51** (R = Bn), **L52** (R = Me)]

The *ee* values of the products given in Scheme 67 indicate that the maximum *ee* value, as in the reactions discussed earlier [see Schemes 48, 51, 54 (X = CH), 55, 57, 60, 61, 63, 66] does not exceed 65%. The C_2 symmetry of intermediates determining the asymmetric induction is the only one common feature of these reactions involving chemically different reactants and having different mechanisms. Hence, the low enantioselectivity can be attributed only to this feature.

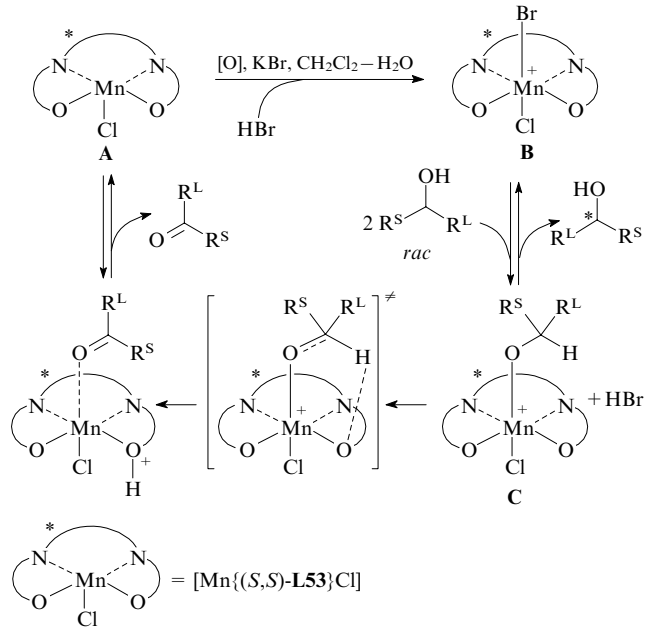
In our opinion, this conclusion is directly supported by the influence of the symmetry of the key intermediate depending on the achiral additional ligand on the enantioselectivity of oxidation of racemic secondary alcohols in the presence of Mn complex with salen ligand (*S*,*S*)-**L53** (Scheme 68).[72]

Scheme 68



Brown *et al.*[72] have proposed a reaction pathway according to which catalytic complex **A** is transformed into asymmetric intermediate **B** in the presence of the [O]−KBr−H_2O system (Scheme 69). This complex is responsible for the asymmetric induction in **B** → **C** step. The replacement of the KBr additional achiral ligand by KCl dramatically decreases the enantioselectivity, as it results in the C_2 symmetry of intermediate **B**.

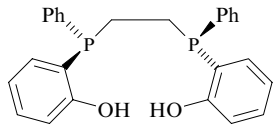
Scheme 69



IV. Enantioselectivity of reactions of substrates coordinated by one, two or three groups in the presence of complexes with C_2-, C_3- and D_2-symmetric chiral ligands

As it was demonstrated earlier,[3, 73] replacement of the alkyl moiety at the double bond of the substrate by a group capable of coordination results in significant increase in the enantioselectivity of hydrogenation of this bond under the

action of rhodium complexes with C_2-symmetric chiral ligands. This conclusion is confirmed by the results of hydrogenation of C=O and C=C bonds catalyzed by complexes of other metals, *e.g.*, ruthenium (Table 1). The difference in the enantioselectivity of reactions of monofunctional (see Table 1, line 1), bifunctional (lines 2–7) and trifunctional (lines 8–11) substrates is evident. A similar difference is also observed in the presence of C_2-symmetric Rh complexes with ligands **L54** and **L2** as catalysts.[3] However, such a great difference in *ee* values of products depending on the ability of substrates to one- or two(three)-point coordination is not observed in the reactions catalyzed by asymmetric complexes.[1] Hydrogenation of bifunctional and especially trifunctional substrates catalyzed by Ru, Rh and Cu complexes with C_2-symmetric ligands is a model reaction that invariably demonstrates high enantioselectivity.[1, 2, 82–97]



L54

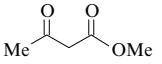
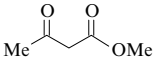
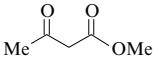
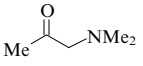
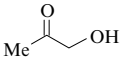
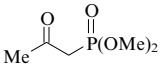
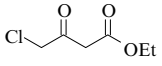
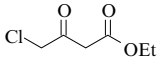
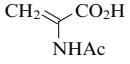
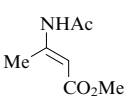
Reactions catalyzed by complexes with C_2-symmetric ligands that demonstrated the highest enantioselectivity are given in Table 2. The reactions are arranged in the order of increasing atomic numbers of metal catalysts. Structural formulas are given only for ligands **L55**–**L77** (in some cases for their complexes), which are not mentioned in Sections II and III.

All the reactions given in Table 2 induced by Li, Mg, Sc, Ti, Ni, Cu, Zn, Y, Ru, Rh and Pd complexes with C_2-symmetric ligands demonstrate high enantioselectivity only in the case of substrates possessing two or three functional groups capable of coordination with metal. If reactants lose one or two of such groups, then the enantioselectivity decreases. This can be clearly seen when comparing reactions given in Schemes 70 and 71.[132, 133] Probably, this is due to the asymmetric intermediate in which the metal coordinates to bifunctional or trifunctional substrate. This regularity may be extended to the reactions with C_3-symmetric complexes (*e.g.*, see the reaction in Scheme 72).[134]

The C_3-symmetric structure of $[Pd_3Zn_3(\mathbf{L80})_3(dba)_3]$ complex (**44**) was proposed[134] on the basis of the results of electron impact mass spectrometry analysis.

Highly enantioselective reactions involving Sc, Ti, Cu, Cr, Rh, Pd, Ir and Au complexes with C_2- and D_2-symmet-

Table 1. Hydrogenation of C=C and C=O bonds of mono-, bi- and trifunctional substrates under the action of ruthenium complexes with ligand **L15**.

No.	Substrate	Complex	Conditions	*ee* of product (%) (configuration)	Ref.
1		[RuBr$_2${(*R*)-**L15**}]	NaOH, Pr^{i}OH, 98 °C	30 (*S*) [a]	49
2		[RuCl$_2${(*R*)-**L15**}]	H_2 (100 atm), MeOH, rt	>99 (*R*)	74
3		[RuCl(η^6-C$_6$H$_6$){(*S*)-**L15**}]Cl	H_2 (100 atm), MeOH, 55 °C	96 (*S*)	75
4		[RuCl(η^6-Cym){(*R*)-**L15**}]Cl [b]	H_2 (100 atm), CH_2Cl_2, 55 °C	93 (*R*)	76
5		[Ru(OAc)$_2${(*S*)-**L15**}]	H_2 (50 atm), MeOH, rt	96 (*S*)	77
6		[RuCl$_2${(*S*)-**L15**}]	H_2 (93 atm), MeOH, rt	92 (*R*)	77
7		[RuCl$_2${(*R*)-**L15**}]·(DMF)$_n$	H_2 (4 atm), MeOH, 25 °C	98 (*R*)	78
8		[Ru(OAc)$_2${(*S*)-**L15**}]	H_2 (100 atm), EtOH, 100 °C	97 (*R*)	79
9		[RuCl(η^6-C$_6$H$_6$)]$_2$–{(*R*)-**L15**}	H_2 (20 atm), EtOH–CH_2Cl_2 (1 : 1), 75 °C	99 (*S*)	76
10		[RuHCl{(*R*)-**L15**}$_2$]	H_2 (2 atm), THF–EtOH (1 : 1), 35 °C	95 (*R*)	80
11		[Ru(OAc)$_2${(*R*)-**L15**}]	H_2 (1 atm), MeOH, 25 °C	96 (*S*)	81

[a] The use of ligand (*S*)-**L31** under the same conditions results in *R*-enantiomer of the product with 15% *ee*; [b] Cym is cymene.

Table 2. Reactions catalyzed by complexes with C_2-symmetric ligands.

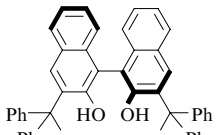
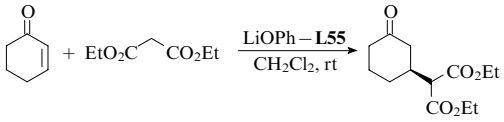
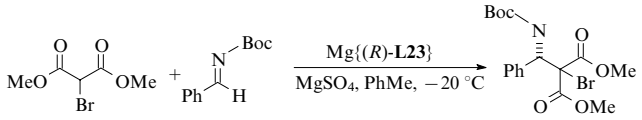
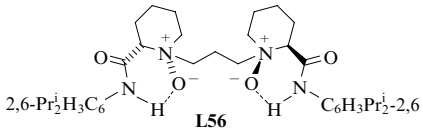
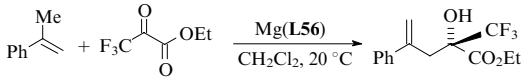
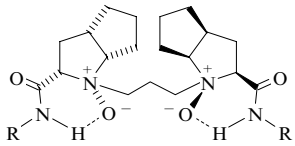
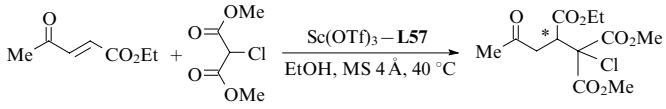
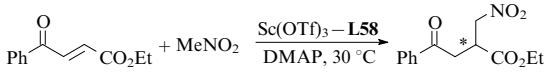
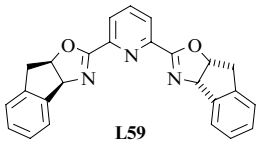
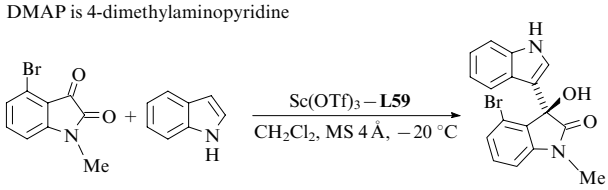
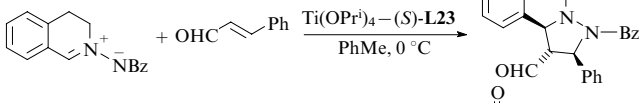
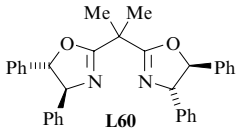
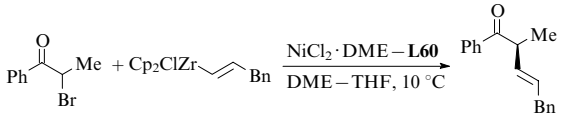
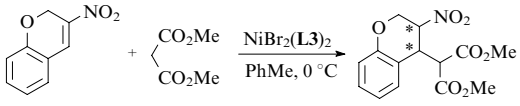
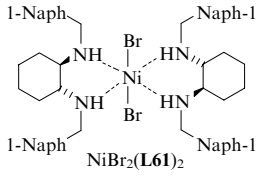
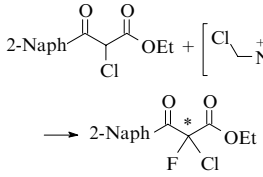
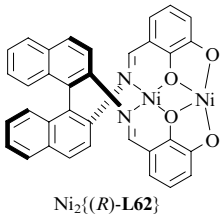
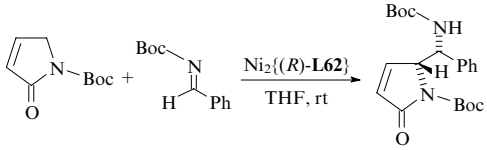
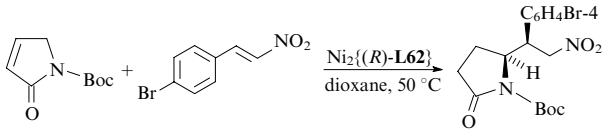
No.	Ligand	Reaction	*ee* (%)	Ref.
1	 **L55**		95 (*S*)	98
2	**L23**		99 (*S*) [a]	99
3	 **L56**		99	100
4	 **L57**, **L58** R = Bn (**L57**), $C_6H_3Pr^i_2$-2,6 (**L58**)		99	101
5		 DMAP is 4-dimethylaminopyridine	98 [b]	101
6	 **L59**		99	102
7	**L23**		99	103
8	 **L60**	 Cp = η^5-C_5H_5	93 (*S*)	104
9	**L3**		95	105
10	 $NiBr_2$(**L61**)$_2$		99	106
11	 Ni_2{(*R*)-**L62**}		99	107
12			99	107

Table 2 (continued).

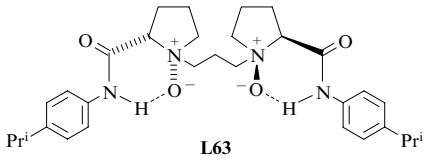
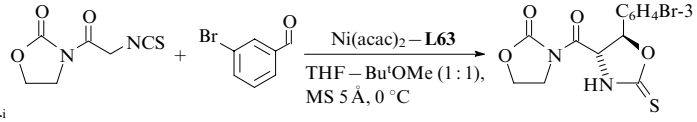
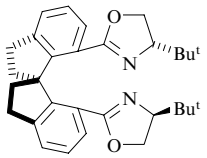
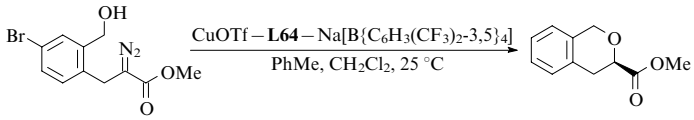
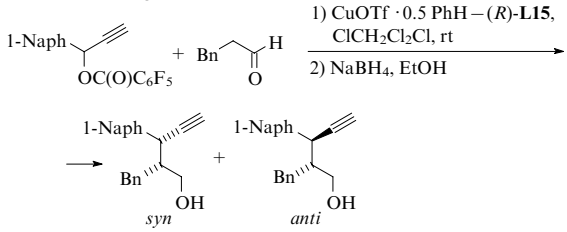
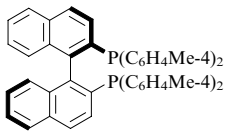
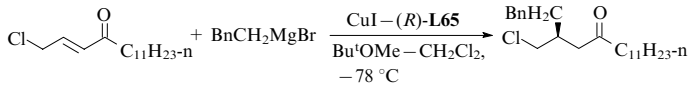
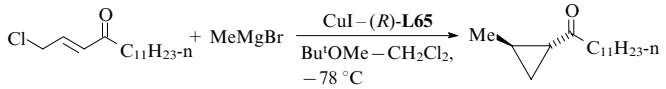
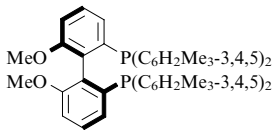
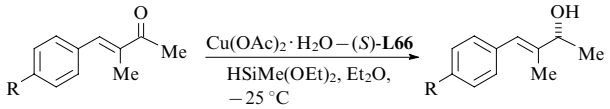
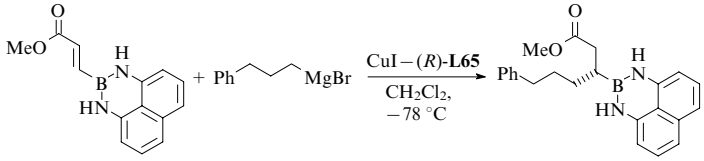
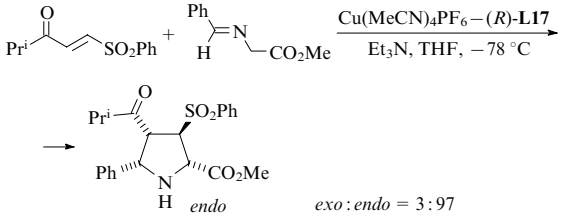
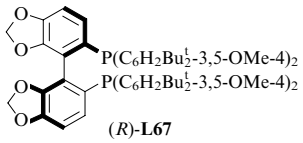
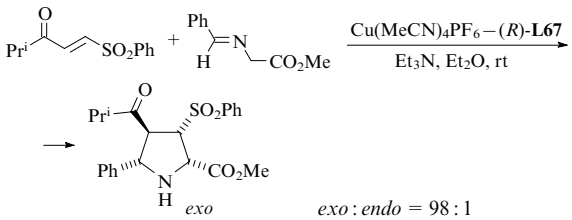
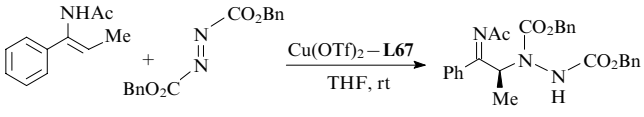
No.	Ligand	Reaction	*ee* (%)	Ref.
13	 **L63**		99	108
14	 (S_a,*S*,*S*)-L**64**		97 (*R*)	109
15	**L15**		99 (*syn*) 96 (*anti*)	110 110
16	 (*R*)-**L65**		96	111
17			98	111
18	 (*S*)-**L66**		90, 93, 95	112
19	**L65**		98.5	113
20	**L17**		99	114
21	 (*R*)-**L67**		> 99	114
22	**L67**		> 91 (*S*)	115

Table 2 (continued).

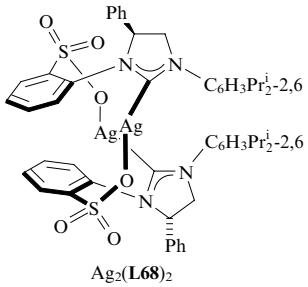
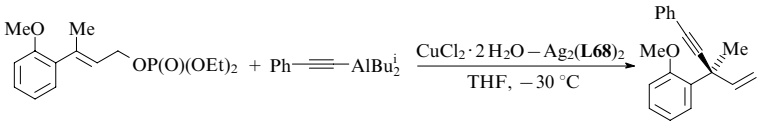
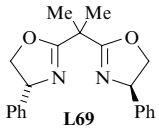
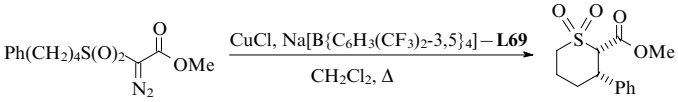
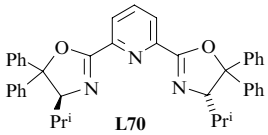
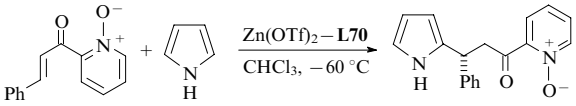
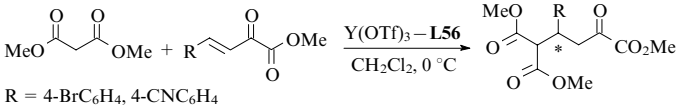
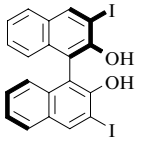
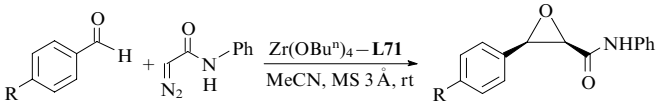
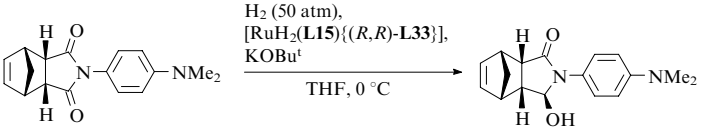
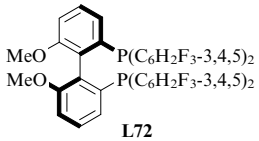
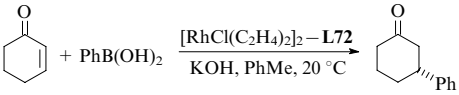
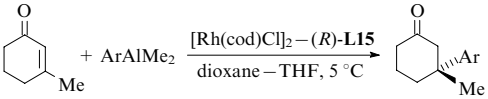
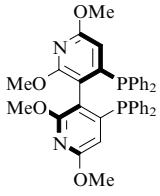
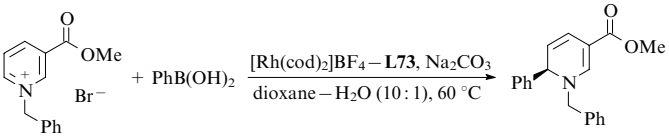
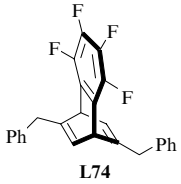
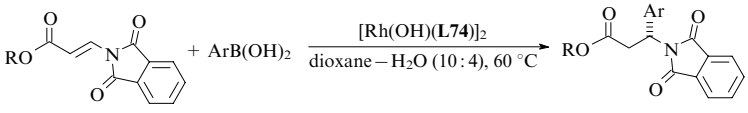
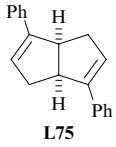
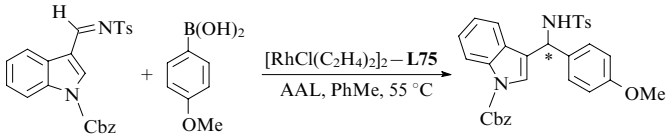
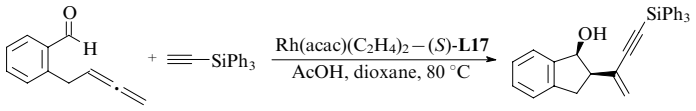
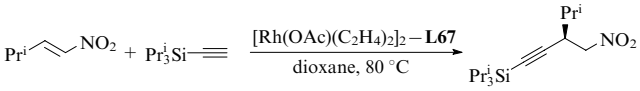
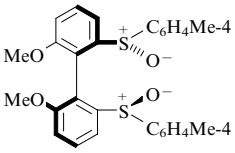
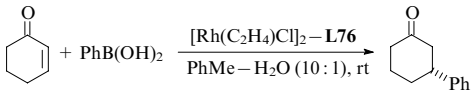
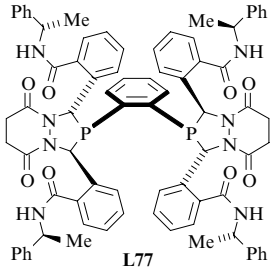
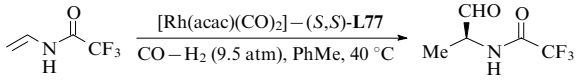
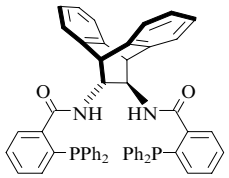
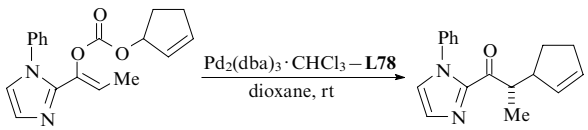
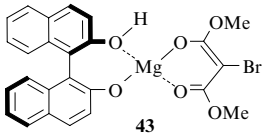
No.	Ligand	Reaction	*ee* (%)	Ref.
23	 Ag_2(**L68**)$_2$	 $CuCl_2 \cdot 2H_2O - Ag_2$(**L68**)$_2$, THF, −30 °C	> 99	116
24	 **L69**	 CuCl, Na[B{$C_6H_3(CF_3)_2$-3,5}$_4$] − **L69**, CH_2Cl_2, Δ	> 99	117
25	 **L70**	 $Zn(OTf)_2$ − **L70**, $CHCl_3$, −60 °C	> 99	118
26	**L56**	 $Y(OTf)_3$ − **L56**, CH_2Cl_2, 0 °C; R = 4-BrC_6H_4, 4-CNC_6H_4	99	119
27	 **L71**	 $Zr(OBu^n)_4$ − **L71**, MeCN, MS 3 Å, rt; R = Br, CN	99	120
28	**L15** + **L33**	 H_2 (50 atm), [RuH_2(**L15**){(*R*,*R*)-**L33**}], $KOBu^t$, THF, 0 °C	97	121
29	 **L72**	 [$RhCl(C_2H_4)_2]_2$ − **L72**, KOH, PhMe, 20 °C	> 99	122
30	**L15**	 [Rh(cod)Cl]$_2$ − (*R*)-**L15**, dioxane − THF, 5 °C; Ar = 3-$CF_3C_6H_4$	99	123
31	 **L73**	 + $PhB(OH)_2$, [Rh(cod)$_2$]BF_4 − **L73**, Na_2CO_3, dioxane − H_2O (10 : 1), 60 °C	99	124
32	 **L74**	 + $ArB(OH)_2$, [Rh(OH)(**L74**)]$_2$, dioxane − H_2O (10 : 4), 60 °C; R = 2,6-$Me_2C_6H_3$; Ar = 3,5-$Me_2C_6H_3$	99	125

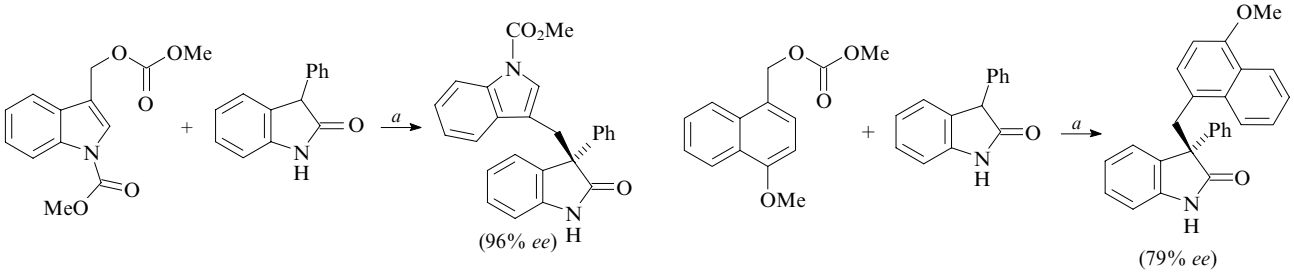
Table 2 (continued).

No.	Ligand	Reaction	*ee* (%)	Ref.
33	 **L75**	 Cbz is benzyloxycarbonyl	97 – 99 [c]	126
34	**L17**	 acac is acetylacetonate	99	127
35	**L67**		99	128
36	 **L76**		99	129
37	 **L77**		99	130
38	 (*R*,*R*)-**L78**	 dba is dibenzylideneacetone	99	131

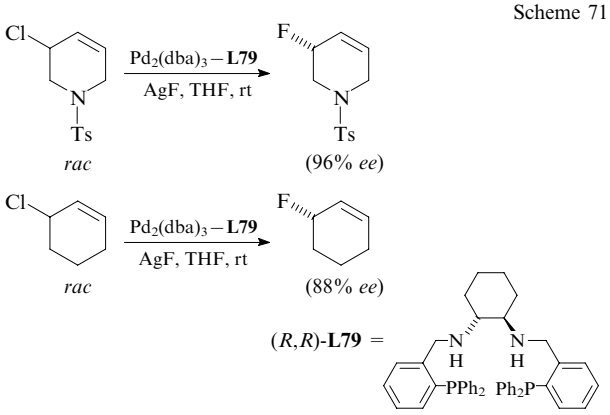
[a] A possible structure of *in situ* obtained magnesium complex with **L23** and methyl malonate (structure **43**) is asymmetric. [b] The *ee* value does not change on the addition of 4-dimethylaminopyridine as the AAL. [c] Et_3N, aqueous KOH, KF, K_3PO_4 and KHF_2 and H_2O were used as the AAL; only in the case of KOH (aq.), the *ee* value decreased to 97%.


43

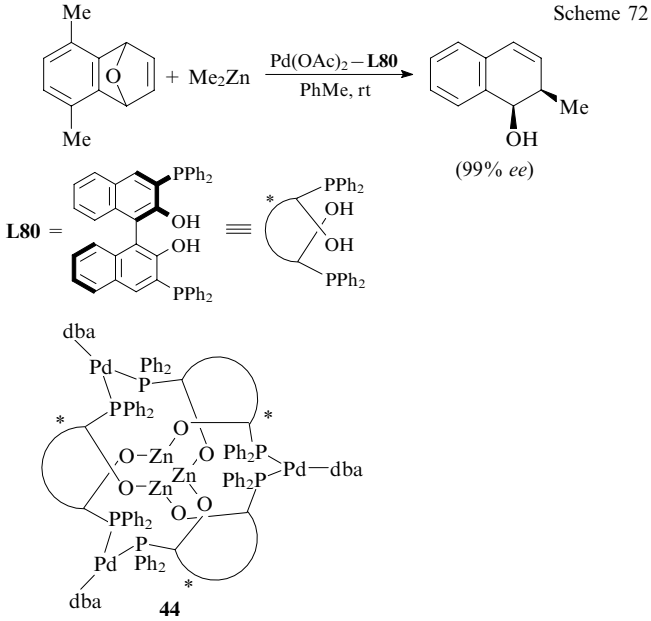
Scheme 70


(*a*) [(η^3-C_3H_5)PdCp] – **L78**, Bu^{t}OH, dioxane, 25 °C

Scheme 71



Scheme 72



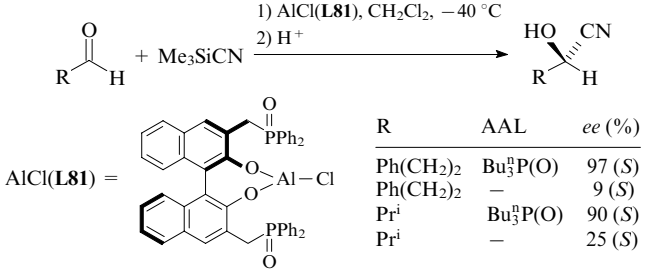
ric ligands should also be mentioned.[135–145] These reactions also obey the stated regularity related to the number ($n \geqslant 2$) of coordinating groups of substrate. However, exceptions are known.[146–149] Probably, they are due to replacement of the coordination of tetradentate C_2-symmetric ligand by the coordination of its bidentate asymmetric half.

The enantioselectivity of some reactions (see, *e.g.*, lines 5 and 33 in Table 2) does not depend on additional achiral ligands. In some papers with the use of additional achiral ligands (see Table 2, lines 20 and 21) or molecular sieves (see Table 2, lines 4, 6, 13, 27), no comparative study of the enantioselectivity has been carried out. However, it is known that additional achiral ligands and molecular sieves have a favourable impact on the enantioselectivity.

V. Dependence of the enantioselectivity of reactions catalyzed by C_2-symmetric complexes on additional achiral ligands and molecular sieves

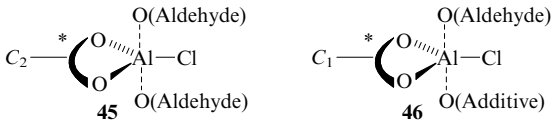
In a series of catalytic reactions an increase in the enantioselectivity is observed in the presence of additional achiral ligands or additional catalysts (co-catalysts).[1,2,150] Cyanosilylation reaction of aldehydes induced by complex AlCl(**L81**) is a typical example (Scheme 73).[151]

Scheme 73



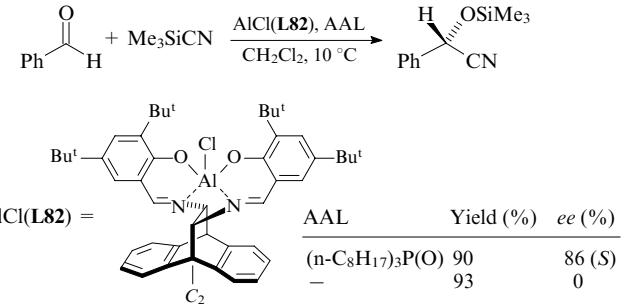
R	AAL	*ee* (%)
$Ph(CH_2)_2$	$Bu^n_3P(O)$	97 (*S*)
$Ph(CH_2)_2$	–	9 (*S*)
Pr^i	$Bu^n_3P(O)$	90 (*S*)
Pr^i	–	25 (*S*)

Trigonal-bipyramidal structures **45** and **46** possessing different symmetry have been proposed as possible intermediates of this reaction.[152,153] Unlike the reaction in the absence of additional achiral ligand, in the presence of such ligand (Additive), intermediate **46** loses the C_2 symmetry axis. This may serve as an explanation of the increase in the enantioselectivity in the presence of AAL.



Another startling example of the sensitivity of enantioselectivity of a catalytic reaction to AAL is represented by cyanosilylation of benzaldehyde in the presence of complex AlCl(**L82**) (Scheme 74).[154]

Scheme 74

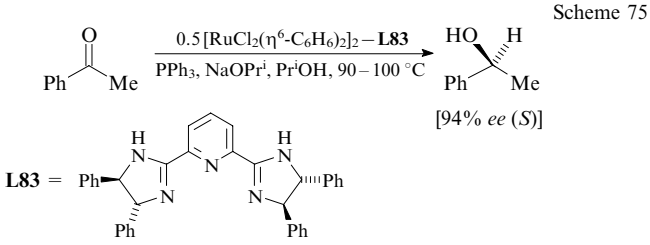


AAL	Yield (%)	*ee* (%)
$(n\text{-}C_8H_{17})_3P(O)$	90	86 (*S*)
–	93	0

The dramatic increase in the enantioselectivity in the presence of additional achiral ligand is probably explained in the same way as in the previous case.

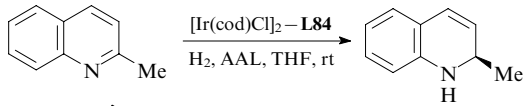
In the hydrogen transfer reaction catalyzed by the ruthenium complex with ligand **L83** (Scheme 75),[155] the addition of PPh_3 into the reaction mixture apparently results in a non-symmetrical geometry of the key intermediate, which accounts for the high enantioselectivity. In the absence of AAL, the *ee* value is only 7%.

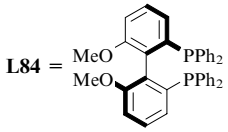
Scheme 75



Another enantioselective reaction depending on the AAL is hydrogenation of quinaldine catalyzed by the iridium complex with ligand **L84** (Scheme 76).[156]

Scheme 76

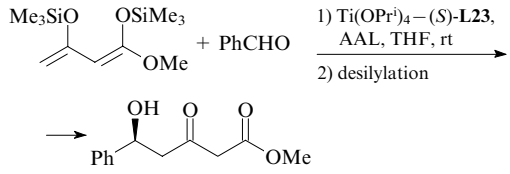


L84 = 

AAL	*ee* (%)
AgOTf	7 (*R*)
AgOTf + HOTf	29 (*S*)
HOTf	79 (*S*)
HOTf + piperidine	86 (*R*)

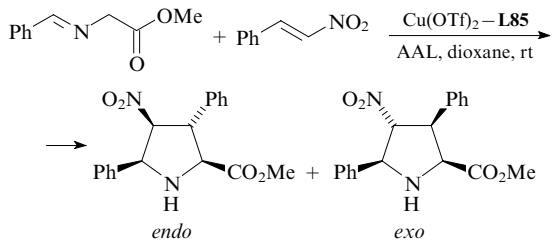
It may be supposed that the dependence of enantioselectivity on the additional achiral ligands is significant only for the reactions of monofunctional substrates (see Schemes 73–76). However, this effect is also tangible for the reactions of substrates that coordinate by two or three groups. In this case, low *ee* value of the product in the absence of AAL is a necessary condition. Aldol condensation in the presence of titanium complex with (*S*)-**L23** (Scheme 77) [157] and [3 + 2]-cycloaddition involving copper complex with **L85** (Scheme 78) [158] may serve as examples.

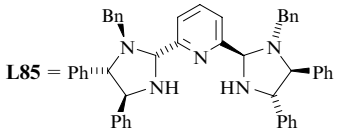
Scheme 77



AAL	*ee* (%)	AAL	*ee* (%)
–	5	Et_3N	74
MS 4 Å	23	$MgCl_2$	85
Pr^iNH_2	52	LiCl	97

Scheme 78



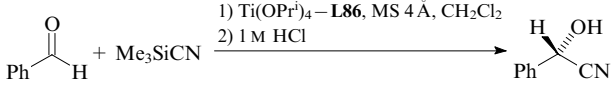
L85 = 

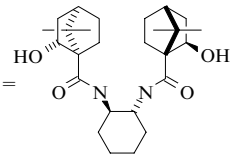
AAL	*endo* : *exo*	*ee* (*endo*) (%)
–	83 : 17	51
Et_3N	96 : 4	74
Cs_2CO_3	99 : 1	99

Meanwhile, some reactions of polyfunctional substrates that are highly enantioselective in the presence of AAL and are catalyzed by Mg,[159] Al,[160] Ca,[161] Sc,[162–164] Ti,[165] Cu,[166–169] Zn,[170] Rh [171–174] and In [175] complexes have not been investigated in the absence of these additional coordinating compounds (ligands).

Molecular sieves also have influence on the enantioselectivity of reactions.[1, 2, 158] The presence of molecular sieves (MS 4 Å, MS 3 Å) in the reaction mixture increases the enantioselectivity of catalytic reactions induced by metal complexes with C_2-symmetric ligands. The addition of trimethylcyanosilane to benzaldehyde (monofunctional substrate) catalyzed by Ti complex with ligand **L86** is an example of this effect (Scheme 79).[176]

Scheme 79



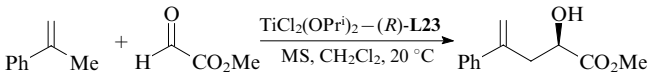
L86 = 

AAL	*T*/°C	*ee* (%)
MS 4 Å	–78	94 (*S*)
–	0	20 (*S*)

It should be noted that in the absence of molecular sieves at –30 °C, the reaction does not proceed at all.

A similar effect is observed in the case of bifunctional substrate in ene reaction involving methyl glyoxylate (Scheme 80).[177] Titanium complex with (*R*)-**L23** acts as the catalyst.

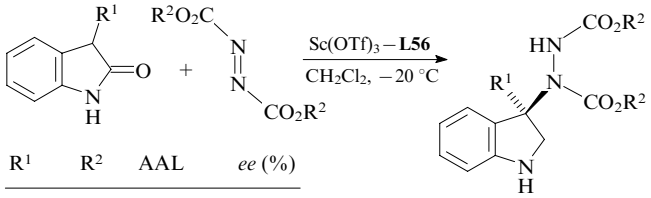
Scheme 80



[95% *ee* (*R*); without MS, 10% *ee*]

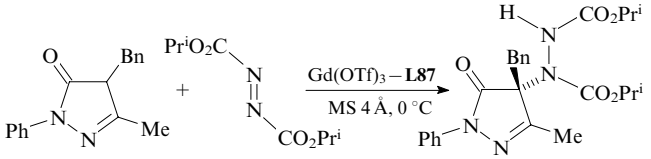
In the case of polyfunctional substrates, the effect is significantly weaker. Thus, in α-amination reactions of 3-substituted 2-oxindoles (Scheme 81) [178] and 4-substituted pyrazolone (Scheme 82) [179] catalyzed by lanthanide complexes with related ligands **L56** and **L87**, respectively, the *ee* value of the product increases only by 2%–8% in the presence of molecular sieves.

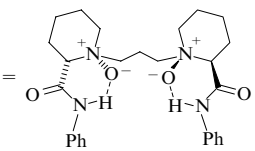
Scheme 81



R^1	R^2	AAL	*ee* (%)
Me	Pr^i	–	90
Me	Pr^i	MS 4 Å	92
Bn	Et	MS 4 Å	98

Scheme 82

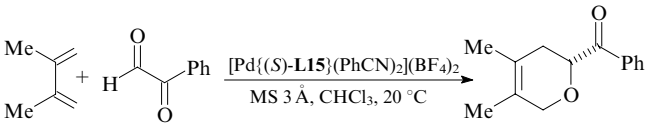


L87 = 

(96% *ee*; wihout MS, 93% *ee*)

As in the case of additional achiral ligand, the increase in the enantioselectivity of the reaction in the presence of molecular sieves may be coused by the loss of C_2-symmetry by key intermediates responsible for asymmetric induction.[1] Indeed, chelate-type metal complexes tend to be adsorbed by the apical vacancies on the chemisorbent surface. If the C_2-symmetry axis lies in the plane of the chelate ring, the complex beng adsorbed loses the symmetry and becomes asymmetric. For example, the Diels–Alder reaction involving the Pd complex with (*S*)-**L15** (Scheme 83)[180] is more enantioselective in the presence of molecular sieves: 96% *ee*, without MS, 79% *ee*.

Scheme 83

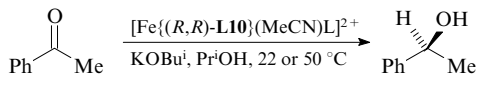


The crystal structure of the complex $[Pd\{(S)\text{-}\mathbf{L15}\}(PhCN)_2](BF_4)_2$ has been studied by X-ray diffraction.[180] The metal atom is coordinated to two phosphorus atoms of the ligand and to two benzonitrile molecules. The complex as a whole has a slighlty distorted square planar geometry and possesses the C_2-symmetry axis. It is highly probable that this planar molecule is adsorbed on the surface of chemisorbent (MS 3 Å) by the apical vacancy of the palladium atom. In this case the C_2-symmetry axis is lost and asymmetric induction is controlled by the asymmetric key intermediate. Unfortunately, most researchers who used molecular sieves in reaction mixtures of asymmetric reactions did not mention reference reactions without molecular sieves.[181–188]

VI. Comparison of the enantioselectivities of reactions in the presence of complexes of the same metal with C_2- and C_1-symmetric ligands of similar structure and under the same conditions

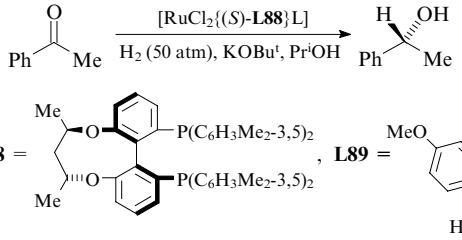
As it was noted earlier, alkylation of aldehydes by dialkylzinc in the presence of chiral ligands [without addition of $Ti(OPr^i)_4$] and hydrogenation with hydrogen transfer of ketones under the action of chiral Rh, Ir and Ru complexes are reactions in which the enantioselectivity is significantly higher in the case of asymmetric catalysts than C_2-symmetric catalysts. For the latter reaction, this is true only for monofunctional substrates.[1,2] This is confirmed by hydrogenation of ketones in the presence of iron complexes with salan (*R*,*R*)-**L10** (Scheme 84)[189] and ruthenium complexes with diphosphine (**L88**) and diamine (**L35** or **L89**) ligands (Scheme 85).[190]

Scheme 84



L	Hydrogenating reagent	T/°C	Catalyst symmetry	*ee* (%)
MeCN	H_2	50	C_2	27 (*S*)
Bu^tCN	Pr^iOH	22	C_1	76 (*S*)

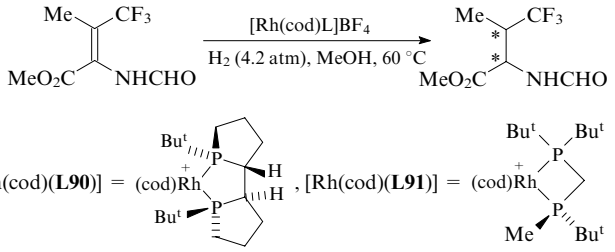
Scheme 85



L	Symmetry of ligand L	*ee* (%)
L35	C_2	91.2
L89	C_1	99.8

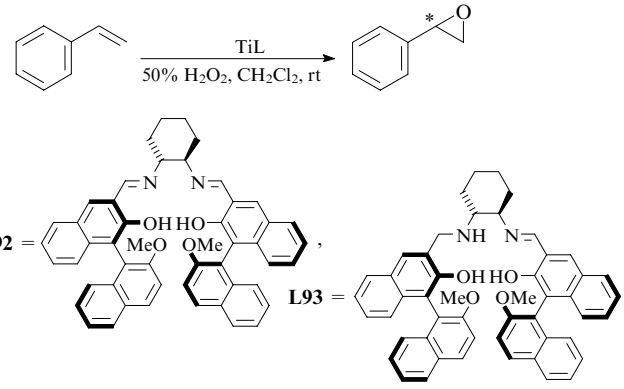
A similar tendency may also be noted for the hydrogenation reactions in the presence of rhodium(I) complexes with diphosphine ligand **L90** or **L91** (Scheme 86)[191] and epoxidation with the participance of titanium complex with salan (**L92**) or salalen (**L93**) ligand (Schem 87).[192]

Scheme 86



L	Symmetry of ligand L	*ee* (%)
L90	C_2	92
L91	C_1	> 99

Scheme 87



L	Symmetry of ligand L	*ee* (%)
L92	C_2	40 (*S*)
L93	C_1	80 (*S*)

50% H_2O_2

The above-mentioned reaction shown in Scheme 68 may serve as direct experimental evidence for the discussed trend. Transition from C_2 to C_1 symmetry of the key

intermediate of this reaction (see Scheme 69) leads to a dramatic increase in *ee* of the product (*ee* < 2 and > 99%, respectively).[72] As demonstrated by the comparison of the results of the reactions given in Schemes 68, 84, 85, 87, with the reaction in Scheme 86, this trend is more pronounced for monofunctional substrates.

VII. Reactions catalyzed by complexes with asymmetric chiral ligands

If a catalyst contains an asymmetric chiral ligand, the reactions proceed with a high enantioselectivity, and no multifunctional substrates, AAL or molecular sieves are needed. This regularity is confirmed by the examples of reactions involving ligands **L94**–**L114** listed in Table 3.

In the reaction of benzaldehyde with dimethyl phosphite (see Table 3, line 8), the catalytic system consists of $Ti(OPr^i)_4$ complex with binaphthyldiol **L71** and cinchonidine (**L100**). Cinchonidine alkaloid forms a bifunctional asymmetric catalyst on the basis of titanium complexes with diols.

It should be particularly noted that hydrogenation of monofunctional substrates of arylalkene type (see Table 3, lines 18, 19) is enantioselective only when catalyzed by iridium complexes with chiral P,N- and N,N-ligands (see also Refs 216 and 217).

The highest enantioselectivity (99% *ee* and higher) has been achieved in the reactions of substrates capable of two- and three-point coordination under the action of Ti,[218] V,[219,220] Co,[221] Ni,[222] Cu,[223–233] Ru,[234–242] Rh,[235,243–257] Pd,[258–264] Ag,[265] In,[266] Re[267] and Ir[235,268–270] complexes with asymmetric chiral ligands. Molecular sieves and additional achiral ligands also favour high enantioselectivity in the reactions of mentioned substrates catalyzed by asymmetric complexes.[271–277] Thus, the degree of enantioselectivity achieved using asymmetric chiral complexes as catalysts exceeds in all types of reactions the degree of enantioselectivity achieved with the participance of C_2-symmetric chiral complexes.

The mechanisms of asymmetric induction of reactions discussed in this Section may be classified as coopera-

Table 3. Reactions of monofunctional substrates catalyzed by complexes with asymmetric ligands.

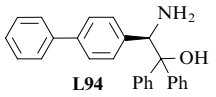
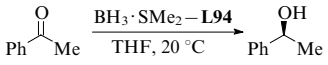
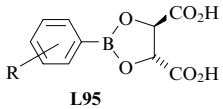
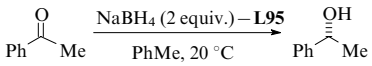
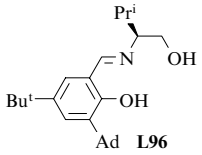
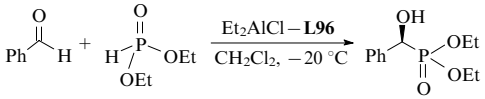
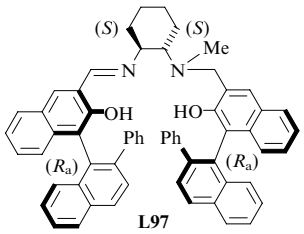
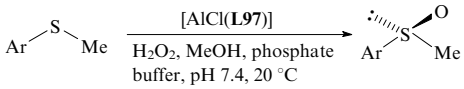
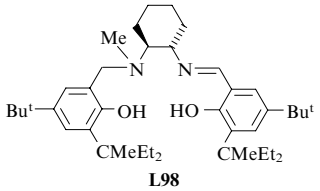
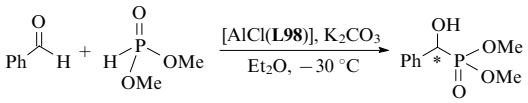
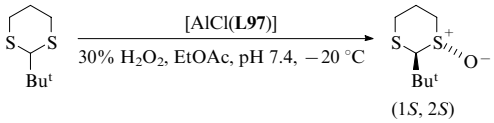
No.	Ligand	Reaction	*ee* (%)	Ref.
1	 **L94**		> 99 (*S*) [a]	193
2	 **L95** R = 3-NO_2, 4-Cl		99 (*S*) [b]	194
3	 **L96** Ad is adamantyl		97 (*S*)	195
4	 **L97**	 Ar = Ph, XC_6H_4 (X = 2-MeO, 4-MeO, 2-Cl, 3-Cl, 4-Cl)	96–99 [c]	196
5	 **L98**		97	197
6	**L97**	 (1*S*, 2*S*)	> 99	198

Table 3 (continued).

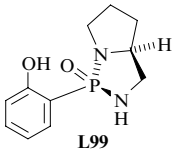
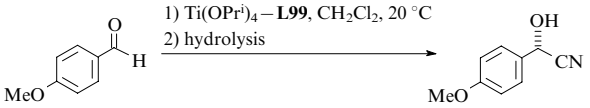
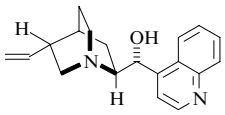
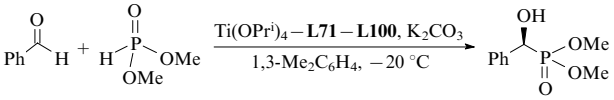
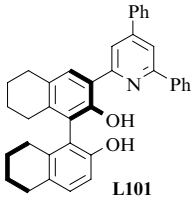
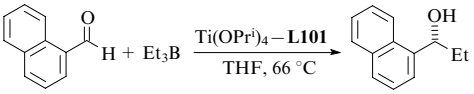
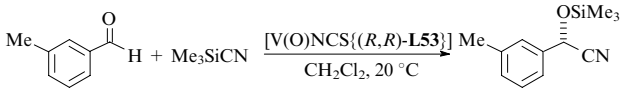
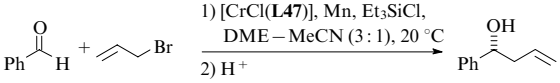
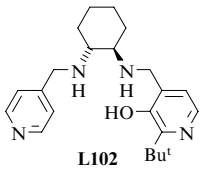
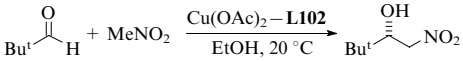
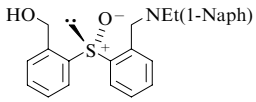
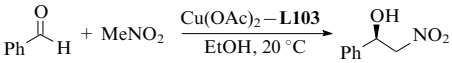
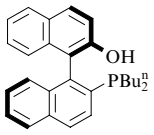
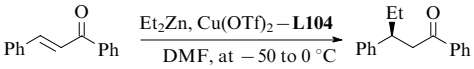
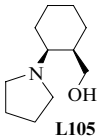
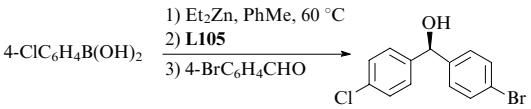
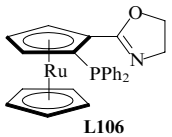
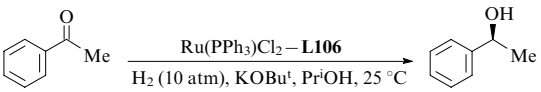
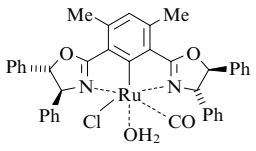
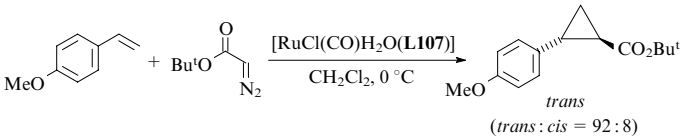
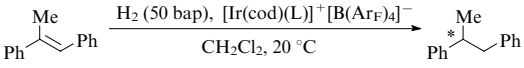
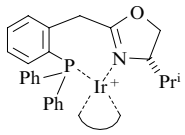
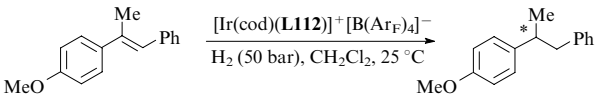
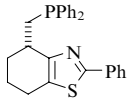
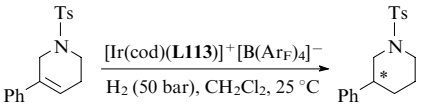
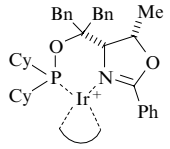
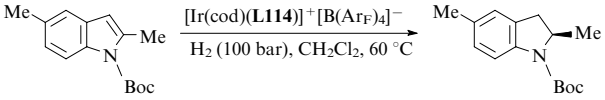
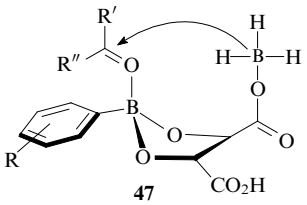
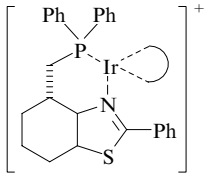
No.	Ligand	Reaction	*ee* (%)	Ref.
7	 **L99**	 1) $Ti(OPr^i)_4$ – **L99**, CH_2Cl_2, 20 °C; 2) hydrolysis	> 98 (*S*)	199
8	**L71**,  **L100**	 $Ti(OPr^i)_4$ – **L71** – **L100**, K_2CO_3; 1,3-$Me_2C_6H_4$, −20 °C	99 (*S*)	200
9	 **L101**	 $Ti(OPr^i)_4$ – **L101**; THF, 66 °C	97 (*R*)	201
10	**L53**	 [V(O)NCS{(*R*,*R*)-**L53**}]; CH_2Cl_2, 20 °C	> 98 (*S*)	202
11	**L47**	 1) [CrCl(**L47**)], Mn, Et_3SiCl, DME – MeCN (3 : 1), 20 °C; 2) H^+	99 (*R*)	203
12	 **L102**	 $Cu(OAc)_2$ – **L102**; EtOH, 20 °C	99 (*R*)	204
13	 **L103**	 $Cu(OAc)_2$ – **L103**; EtOH, 20 °C	98 (*R*)	205
14	 **L104**	 Et_2Zn, $Cu(OTf)_2$ – **L104**; DMF, at −50 to 0 °C	> 99 (*S*)	206
15	 **L105**	 1) Et_2Zn, PhMe, 60 °C; 2) **L105**; 3) 4-BrC_6H_4CHO	> 99 (*R*)	207
16	 **L106**	 $Ru(PPh_3)Cl_2$ – **L106**; H_2 (10 atm), $KOBu^t$, Pr^iOH, 25 °C	> 98 (*S*)	208
17	 [RuCl(CO)(H_2O)(**L107**)]	 [RuCl(CO)H_2O(**L107**)]; CH_2Cl_2, 0 °C; *trans* (*trans* : *cis* = 92 : 8)	99	209

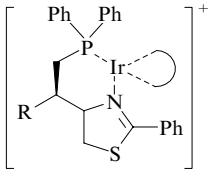
Table 3 (continued).

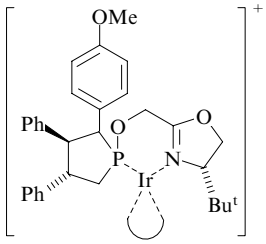
No.	Ligand	Reaction	*ee* (%)	Ref.
18	see [d]	 Ar_F = 3,5-$(CF_3)_2C_6H_3$, L = **L108**–**L111**	96 (*R*)	210–212
19	 [Ir(cod)(**L112**)]$^+$  = cod		97	213
20	 **L113**		97	214
21	 [Ir(cod)(**L114**)]$^+$		>99 (*R*)	215

[a] Oxazaborolidine generated *in situ* serves as the catalyst; [b] structure **47** was proposed as a transition state for this reaction; [c] the highest *ee* value (>99%) was achieved for Ar = 2-ClC_6H_4; [d] ligands **L108**–**L111** (= cod)


47


[Ir(cod)(**L108**)]$^+$


[Ir(cod)(L)]$^+$
(R = Me, L = **L109**;
R = Bn, L = **L110**)


[Ir(cod)(**L111**)]$^+$

tive[271,278,279] and stepwise[273,280–282] in terms of the general mechanisms proposed by the authors.

VIII. Conclusion

More than 250 asymmetric reactions catalyzed by chiral metal complexes with enantiomeric excess of the product approaching 99.9% (Ref.283) have been considered in the present review. Relying on the hypotheses expressed earlier,[1,2] on the basis of contemporary experimental data, the authors tried to reveal and formulate the most important factors that influence the asymmetric induction for the highest enantioselectivity. It has been shown that two factors have a particularly great impact on the asymmetric induction and the enantioselectivity: one- or two(three)-point coordination of the substrate and C_1- or C_2-symmetry of the key intermediate responsible for asymmetric induction. In the case of reactions of simple monofunctional substrates that are coordinated to only one (reacting) group (one-point adsorption), the high degree of freedom of binding of such substrates restricts the structure and symmetry of the catalytic complex.[2] If the intermediate that controls asymmetric induction preserves the symmetry of the starting complex, then better enantioselectivity is expected of the complexes with asymmetric ligands than the complexes containing C_2-symmetric ligands. The C_2 symmetry of the key intermediate of such processes may be responsible for the low enantioselectivity (*ee* <65%) of reactions given in Schemes 48, 51, 54 (X = CH), 55, 57, 60–63, 66 and 67. The enantioselectivity of reactions of the substrates possessing two or three functional groups does not depend on the symmetry of the catalytic complex. This may be explained by the fact that in the transformations induced by C_2-symmetric chiral complexes, the symmetry is being lost at the step that precedes the asymmetric induction. Achiral additional ligands and molecular sieves increase the enantioselectivity of the reactions in the presence of complexes with C_2-symmetric ligands. They favour the loss of symmetry by the intermediate responsible for the asymmetric induction.

The asymmetric induction may comprise two(three) intermediate steps (stepwise mechanism; see Section II.1) or one step (cooperative mechanism; see Section II.2).

On average, the degree of enantioselectivity achieved with the use of asymmetric chiral complexes in all types of reactions slightly exceeds the degree of enantioselectivity achieved with the help of C_2-symmetric chiral complex catalysts.

References

1. V A Pavlov *Tetrahedron* **64** 1147 (2008)
2. V A Pavlov, T N Pavlova *Russ. Chem. Rev.* **79** 881 (2010) [*Usp. Khim.* **79** 961 (2010)]
3. V A Pavlov *Russ. Chem. Rev.* **70** 1037 (2001) [*Usp. Khim.* **70** 1175 (2001)]
4. C R Landis, J Halpern *J. Am. Chem. Soc.* **109** 1746 (1987)
5. I D Gridnev, N Higashi, K Asakura, T Imamoto *J. Am. Chem. Soc.* **122** 7183 (2000)
6. V A Pavlov *Russ. Chem. Rev.* **71** 33 (2002) [*Usp. Khim.* **71** 39 (2002)]
7. H Egami, K Matsumoto, T Oguma, T Kunisu, T Katsuki *J. Am. Chem. Soc.* **132** 13633 (2010)
8. R K Sharma, T V RajanBaby *J. Am. Chem. Soc.* **132** 3295 (2010)
9. A Nakamura, S Lectard, D Hashizume, Y Hamashima, M Sodeoka *J. Am. Chem. Soc.* **132** 4036 (2010)
10. R Yazaki, N Kumagai, M Shibasaki *J. Am. Chem. Soc.* **132** 10275 (2010)
11. R Yazaki, N Kumagai, M Shibasaki *J. Am. Chem. Soc.* **132** 5522 (2010)
12. D R Fandrick, K R Fandrick, J T Reeves, Z Tan, W Tang, A G Capacci, S Rodriguez, J J Song, H Lee, N K Yee, C H Senanayake *J. Am. Chem. Soc.* **132** 7600 (2010)
13. G Hattori, K Sakata, H Matsuzawa, Y Tanabe, Y Miyake, Y Nishibayashi *J. Am. Chem. Soc.* **132** 10592 (2010)
14. I-H Chen, M Kanai, M Shibasaki *Org. Lett.* **12** 4098 (2010)
15. W Li, G Hou, C Wang, Y Jiang, X Zhang *Chem. Commun.* **46** 3979 (2010)
16. R Noyori, M Yamakawa, S Hashiguchi *J. Org. Chem.* **66** 7931 (2001)
17. S Takebayashi, N Dabral, M Miskolzie, S H Bergens *J. Am. Chem. Soc.* **133** 9666 (2011)
18. C Schotes, A Mezzetti *J. Am. Chem. Soc.* **132** 3652 (2010)
19. A DeAngelis, V W Shurtleff, O Dmitrenko, J M Fox *J. Am. Chem. Soc.* **133** 1650 (2011)
20. T Nishimura, H Makino, M Nagaosa, T Hayashi *J. Am. Chem. Soc.* **132** 12865 (2010)
21. Y Wang, X Hu, H Du *Org. Lett.* **12** 5482 (2010)
22. F Menard, D Perez, D S Roman, T M Chapman, M Lautens *J. Org. Chem.* **75** 4056 (2010)
23. A M R Smith, H S Rzepa, A J P White, D Billen, K K (Mimi)Hii *J. Org. Chem.* **75** 3085 (2010)
24. J-J Feng, X-F Chen, M Shi, W-L Duan *J. Am. Chem. Soc.* **132** 5562 (2010)
25. K Aikawa, Y Hioki, K Mikami *Org. Lett.* **12** 5716 (2010)
26. K Aikawa, Y Hioki, N Shimizu, K Mikami *J. Am. Chem. Soc.* **133** 20092 (2011)
27. A Yanagisawa, S Takeshita, Y Izumi, K Yoshida *J. Am. Chem. Soc.* **132** 5328 (2010)
28. T Yukawa, B Seelig, Y Xu, H Morimoto, S Matsunaga, A Berkessel, M Shibasaki *J. Am. Chem. Soc.* **132** 11988 (2010)
29. Y Liu, D Shang, X Zhou, Y Zhu, L Lin, X Liu, X Feng *Org. Lett.* **12** 180 (2010)
30. T Wang, Y Liang, Z-X Yu *J. Am. Chem. Soc.* **133** 9343 (2011)
31. M Hatano, T Horibe, K Ishihara *J. Am. Chem. Soc.* **132** 56 (2010)
32. W Zheng, Z Zhang, M J Kaplan, J C Antilla *J. Am. Chem. Soc.* **133** 3339 (2011)
33. Z Zhang, W Zheng, J C Antilla *Angew. Chem., Int. Ed.* **50** 1135 (2011)
34. G Wang, J Zhao, Y Zhou, B Wang, J Qu *J. Org. Chem.* **75** 5326 (2010)
35. Y-Y Han, Z-J Wu, W-B Chen, X-L Du, X-M Zhang, W-C Yuan *Org. Lett.* **13** 5064 (2011)
36. S Barroso, G Blay, M C Muñoz, J R Pedro *Org. Lett.* **13** 402 (2011)
37. J Wu, X Li, F Wu, B Wan *Org. Lett.* **13** 4834 (2011)
38. D Zhao, L Mao, D Yang, R Wang *J. Org. Chem.* **75** 6756 (2010)
39. D Zhao, L Mao, Y Wang, D Yang, Q Zhang, R Wang *Org. Lett.* **12** 1880 (2010)
40. R Tanaka, K Noguchi, K Tanaka *J. Am. Chem. Soc.* **132** 1238 (2010)
41. R Shintani, M Takeda, Y-T Soh, T Ito, T Hayashi *Org. Lett.* **13** 2977 (2011)
42. C-M Chao, D Beltrami, P Y Toullec, V Michelet *Chem. Commun.* 6988 (2009)
43. Z Li, H Yamamoto *J. Am. Chem. Soc.* **132** 7878 (2010)
44. R Noyori, S Hashiguchi *Acc. Chem. Res.* **30** 97 (1997)
45. M J Palmer, M Wills *Tetrahedron: Asymmetry* **10** 2045 (1999)
46. G Zassinovich, G Mestroni, S Gladiali *Chem. Rev.* **92** 1051 (1992)
47. P Gamez, F Fache, P Mangeney, M Lemaire *Tetrahedron Lett.* **34** 6897 (1993)
48. R Spogliarich, J Kašpar, M Graziani, F Morandini *J. Organomet. Chem.* **306** 407 (1986)
49. J-P Genêt, V Ratovelomanana-Vidal, C Pinel *Synlett* 478 (1993)
50. P Gamez, F Fache, M Lemaire *Tetrahedron: Asymmetry* **6** 705 (1995)
51. K Murata, T Ikariya, R Noyori *J. Org. Chem.* **64** 2186 (1999)
52. C A Sandoval, T Ohkuma, K Muñiz, R Noyori *J. Am. Chem. Soc.* **125** 13490 (2003)
53. R J Hamilton, C G Leong, G Bigam, M Miskolzie, S H Bergens *J. Am. Chem. Soc.* **127** 4152 (2005)
54. K Abdur-Rashid, M Faatz, A J Lough, R H Morris *J. Am. Chem. Soc.* **123** 7473 (2001)
55. M Bernard, F Delbecq, P Sautet, F Fache, M Lemaire *Organometallics* **19** 5715 (2000)
56. A Naik, T Maji, O Reiser *Chem. Commun.* **46** 4475 (2010)
57. S J Li, Y Yiang, A Mi *Tetrahedron: Asymmetry* **3** 1467 (1992)
58. K Soai, A Ookawa, T Kaba, K Ogawa *J. Am. Chem. Soc.* **109** 7111 (1987)
59. X Yang, J Shen, C Da, R Wang, M C K Choi, L Yang, K-y Wong *Tetrahedron: Asymmetry* **10** 133 (1999)
60. K Ding, A Ishii, K Mikami *Angew. Chem., Int. Ed.* **38** 497 (1999)
61. Š Vyskočil, S Jaracz, M Smrčina, M Štícha, V Hanuš, M Polášek, P Kočovský *J. Org. Chem.* **63** 7727 (1998)
62. D Le Goanvich, M Holler, P Pale *Tetrahedron: Asymmetry* **13** 119 (2002)
63. T Rosner, P J Sears, W A Nugent, D G Blackmond *Org. Lett.* **2** 2511 (2000)
64. H Li, C-S Da, Y-H Xiao, X Li, Y-N Su *J. Org. Chem.* **73** 7398 (2008)
65. M Wu, B Wang, S Wang, C Xia, W Sun *Org. Lett.* **11** 3622 (2009)
66. D L Usanov, H Yamamoto *Angew. Chem., Int. Ed.* **49** 8169 (2010)
67. H Egami, T Oguma, T Katsuki *J. Am. Chem. Soc.* **132** 5886 (2010)
68. S Yoshida, K Fukui, S Kikuchi, T Yamada *J. Am. Chem. Soc.* **132** 4072 (2010)
69. E Bergin, D L Hughes, C J Richards *Tetrahedron: Asymmetry* **21** 1619 (2010)
70. S-H Cao, M Shi *Tetrahedron: Asymmetry* **21** 2675 (2010)
71. R Zhang, Q Xu, X Zhang, T Zhang, M Shi *Tetrahedron: Asymmetry* **21** 1928 (2010)

72. M K Brown, M M Blewett, J R Colombe, E J Corey *J. Am. Chem. Soc.* **132** 11165 (2010)
73. B D Vineyard, W S Knowles, M J Sabacky, G L Bachman, D J Weinkauff *J. Am. Chem. Soc.* **99** 5946 (1977)
74. R Noyori, T Ohkuma, M Kitamura, H Takaya, N Sayo, H Kumobayashi, S Akutagawa *J. Am. Chem. Soc.* **109** 5856 (1987)
75. K Mashima, K-h Kusano, N Sato, Y-i Matsumura, K Nozaki, H Kumobayashi, N Sayo, Y Hori, T Ishizaki *J. Org. Chem.* **59** 3064 (1994)
76. V A Pavlov, E V Starodubtseva, M G Vinogradov, V A Ferapontov, O R Malyshev, G L Khais *Izv. Akad. Nauk, Ser. Khim.* 725 (2000) [a]
77. M Kitamura, T Ohkuma, S Inoue, N Sayo, H Kumobayashi, S Akutagawa, T Ohta, H Takaya, R Noyori *J. Am. Chem. Soc.* **110** 629 (1988)
78. M Kitamura, M Tokunaga, R Noyori *J. Am. Chem. Soc.* **117** 2931 (1995)
79. M Kitamura, T Ohkuma, H Takaya, R Noyori *Tetrahedron Lett.* **29** 1555 (1988)
80. H Kawano, T Ikariya, Y Ishii, M Saburi, S Yoshikawa, Y Uchida, H Kumobayashi *J. Chem. Soc., Perkin Trans. 1* 1571 (1989)
81. W D Lubell, M Kitamura, R Noyoi *Tetrahedron: Asymmetry* **2** 543 (1991)
82. B J Flowers, R Gautreau-Service, P G Jessop *Adv. Synth. Catal.* **350** 2947 (2008)
83. X Sun, W Li, G Hou, L Zhou, X Zhang *Adv. Synth. Catal.* **351** 2553 (2009)
84. C-J Wang, C-B Wang, D Chen, G Yang, Z Wu, X Zhang *Tetrahedron Lett.* **50** 1038 (2009)
85. L Qiu, F Y Kwong, J Wu, W H Lam, S Chan, W-Y Yu, Y-M Li, R Guo, Z Zhou, A S C Chan *J. Am. Chem. Soc.* **128** 5955 (2006)
86. C-J Wang, F Gao, G Liang *Org. Lett.* **10** 4711 (2008)
87. D A Rankic, J M Hopkins, M Parvez, B A Keay *Synlett* 2513 (2009)
88. K Kurihara, Y Yamamoto, N Miyaura *Tetrahedron Lett.* **50** 3158 (2009)
89. Y Zou, H Geng, W Zhang, S Yu, X Zhang *Tetrahedron Lett.* **50** 5777 (2009)
90. X Sun, W Li, L Zhou, X Zhang *Adv. Synth. Catal.* **352** 1150 (2010)
91. K Tamura, M Sugiya, K Yoshida, A Yanagisawa, T Imamoto *Org. Lett.* **12** 4400 (2010)
92. X Zhang, K Huang, G Hou, B Cao, X Zhang *Angew. Chem., Int. Ed.* **49** 6421 (2010)
93. B Zupančič, B Mohar, M Stephan *Org. Lett.* **12** 1296 (2010)
94. H Geng, K Huang, T Sun, W Li, X Zhang, L Zhou, W Wu, X Zhang *J. Org. Chem.* **76** 332 (2011)
95. K Mikami, T Murase, L Zhai, Y Itoh, S Ito *Tetrahedron: Asymmetry* **21** 1158 (2010)
96. Z Wu, T Ayad, V Ratovelomanana-Vidal *Org. Lett.* **13** 3782 (2011)
97. Y Wu, S-B Qi, F-F Wu, X-C Zhang, M Li, J Wu, A S C Chan *Org. Lett.* **13** 1754 (2011)
98. Y N Belokon, Z T Gugkaeva, V I Maleev, M A Moskalenko, A T Tsaloev, V N Khrustalev, K V Hakobyan *Tetrahedron: Asymmetry* **22** 167 (2011)
99. M Hatano, T Horibe, K Ishihara *Org. Lett.* **12** 3502 (2010)
100. K Zheng, Y Yang, J Zhao, C Yin, L Lin, X Liu, X Feng *Chem. – Eur. J.* **16** 9969 (2010)
101. Z Wang, D Chen, Z Yang, S Bai, X Liu, L Lin, X Feng *Chem. – Eur. J.* **16** 10130 (2010)
102. N V Hanhan, A H Sahin, T W Chang, J C Fettinger, A K Franz *Angew. Chem., Int. Ed.* **49** 744 (2010)
103. T Hashimoto, Y Maeda, M Omote, H Nakatsu, K Maruoka *J. Am. Chem. Soc.* **132** 4076 (2010)
104. S Lou, G C Fu *J. Am. Chem. Soc.* **132** 5010 (2010)
105. W-Y Chen, L Ouyang, R-Y Chen, X-S Li *Tetrahedron Lett.* **51** 3972 (2010)
106. S H Kang, D Y Kim *Adv. Synth. Catal.* **352** 2783 (2010)
107. N E Shepherd, H Tanabe, Y Xu, S Matsunaga, M Shibasaki *J. Am. Chem. Soc.* **132** 3666 (2010)
108. X Chen, Y Zhu, Z Qiao, M Xie, L Lin, X Liu, X Feng *Chem. – Eur. J.* **16** 10124 (2010)
109. S-F Zhu, X-G Song, Y Li, Y Cai, Q-L Zhou *J. Am. Chem. Soc.* **132** 16374 (2010)
110. A Yoshida, M Ikeda, G Hattori, Y Miyake, Y Nishibayashi *Org. Lett.* **13** 592 (2011)
111. T den Hartog, A Rudolph, B Maciá, A J Minnaard, B L Feringa *J. Am. Chem. Soc.* **132** 14349 (2010)
112. R Moser, Z V Bošković, C S Crowe, B H Lipshutz *J. Am. Chem. Soc.* **132** 7852 (2010)
113. J C H Lee, D G Hall *J. Am. Chem. Soc.* **132** 5544 (2010)
114. R Robles-Machín, M González-Esguevillas, J Adrio, J C Carretero *J. Org. Chem.* **75** 233 (2010)
115. L Chang, Y Kuang, B Qin, X Zhou, X Liu, L Lin, X Feng *Org. Lett.* **12** 2214 (2010)
116. J A Dabrowski, F Gao, A H Hoveyda *J. Am. Chem. Soc.* **133** 4778 (2011)
117. C J Flynn, C J Elcoate, S E Lawrence, A R Maguire *J. Am. Chem. Soc.* **132** 1184 (2010)
118. P K Singh, V K Singh *Org. Lett.* **12** 80 (2010)
119. L Zhou, L Lin, W Wang, J Ji, X Liu, X Feng *Chem. Commun.* **46** 3601 (2010)
120. L He, W-J Liu, L Ren, T Lei, L-Z Gong *Adv. Synth. Catal.* **352** 1123 (2010)
121. S Takebayashi, J M John, S H Bergens *J. Am. Chem. Soc.* **132** 12832 (2010)
122. T Korenaga, R Maenishi, K Hayashi, T Sakai *Adv. Synth. Catal.* **352** 3247 (2010)
123. C Hawner, D Müller, L Gremaud, A Felouat, S Woodward, A Alexakis *Angew. Chem., Int. Ed.* **49** 7769 (2010)
124. C Nadeau, S Aly, K Belyk *J. Am. Chem. Soc.* **133** 2878 (2011)
125. T Nishimura, J Wang, M Nagaosa, K Okamoto, R Shintani, F-y Kwong, W-y Yu, A S C Chan, T Hayashi *J. Am. Chem. Soc.* **132** 464 (2010)
126. H-Y Yang, M-H Xu *Chem. Commun.* **46** 9223 (2010)
127. X-X Guo, T Sawano, T Nishimura, T Hayashi *Tetrahedron: Asymmetry* **21** 1730 (2010)
128. T Nishimura, T Sawano, S Tokuji, T Hayashi *Chem. Commun.*, **46** 6837 (2010)
129. Q-A Chen, X Dong, M-W Chen, D-S Wang, Y-G Zhou, Y-X Li *Org. Lett.* **12** 1928 (2010)
130. R I McDonald, G W Wong, R P Neupane, S S Stahl, C R Landis *J. Am. Chem. Soc.* **132** 14027 (2010)
131. B M Trost, K Lehr, D J Michaelis, J Xu, A K Buckl *J. Am. Chem. Soc.* **132** 8915 (2010)
132. B M Trost, L C Czabaniuk *J. Am. Chem. Soc.* **132** 15534 (2010)
133. M H Katcher, A G Doyle *J. Am. Chem. Soc.* **132** 17402 (2010)
134. K Endo, K Tanaka, M Ogawa, T Shibata *Org. Lett.* **13** 868 (2011)
135. S Bonollo, D Lanari, F Pizzo, L Vaccaro *Org. Lett.* **13** 2150 (2011)
136. J Majer, P Kwiatkowski, J Jurczak *Org. Lett.* **13** 5944 (2011)
137. J D White, S Shaw *Org. Lett.* **13** 2488 (2011)
138. F Berhal, O Esseiva, C-H Martin, H Tone, J-P Genet, T Ayad, V Ratovelomanana-Vidal *Org. Lett.* **13** 2806 (2011)
139. K Masuda, N Sakiyama, R Tanaka, K Noguchi, K Tanaka *J. Am. Chem. Soc.* **133** 6918 (2011)
140. C Qin, V Boyarskikh, J H Hansen, K I Hardcastle, D G Musaev, H M L Davies *J. Am. Chem. Soc.* **133** 19198 (2011)
141. B M Trost, D A Thaisrivongs, J Hartwig *J. Am. Chem. Soc.* **133** 12439 (2011)

142. L Liu, N Isida, S Ashida, M Murakami *Org. Lett.* **13** 1666 (2011)
143. W-J Tang, J Tan, L-J Xu, K-H Lam, Q-H Fan, A S C Chan *Adv. Synth. Catal.* **352** 1055 (2010)
144. G Hou, W Li, M Ma, Xia Zhang, Xum Zhang *J. Am. Chem. Soc.* **132** 12844 (2010)
145. M Murai, J Uenishi, M Uemura *Org. Lett.* **12** 4788 (2010)
146. T Shibata, M Otomo, K Endo *Synlett* 1235 (2010)
147. M Kobayashi, T Suda, K Noguchi, K Tanaka *Angew. Chem., Int. Ed.* **50** 1664 (2011)
148. Y Qu, L Jing, Z Wu, D Wu, X Zhou *Tetrahedron: Asymmetry* **21** 187 (2010)
149. W Jin, X Li, B Wan *J. Org. Chem.* **76** 484 (2011)
150. E M Vogl, H Gröger, M Shibasaki *Angew. Chem., Int. Ed.* **38** 1570 (1999)
151. Y Hamashima, D Sawada, M Kanai, M Shibasaki *J. Am. Chem. Soc.* **121** 2641 (1999)
152. T Ooi, N Kagoshima, K Maruoka *J. Am. Chem. Soc.* **119** 5754 (1997)
153. M Murakata, T Jono, Y Mizuno, O Hoshino *J. Am. Chem. Soc.* **119** 11713 (1997)
154. Z Zeng, G Zhao, Z Zhou, C Tang *Eur. J. Org. Chem.* 1615 (2008)
155. S Enthaler, B Hagemann, S Bhor, G Anilkumar, M K Tse, B Bitterlich, K Junge, G Erre, M Beller *Adv. Synth. Catal.* **349** 853 (2007)
156. D-S Wang, Y-G Zhou *Tetrahedron Lett.* **51** 3014 (2010)
157. Q Xu, J Yu, F Han, J Hu, W Chen, L Yang *Tetrahedron: Asymmetry* **21** 156 (2010)
158. T Arai, A Mishiro, N Yokoyama, K Suzuki, H Sato *J. Am. Chem. Soc.* **132** 5338 (2010)
159. L Lin, J Zhang, X Ma, X Fu, R Wang *Org. Lett.* **13** 6410 (2011)
160. J P Abell, H Yamamoto *J. Am. Chem. Soc.* **131** 15118 (2009)
161. T Poisson, Y Yamashita, S Kobayashi *J. Am. Chem. Soc.* **132** 7890 (2010)
162. W Li, X Liu, X Hao, X Hu, Y Chu, W Cao, S Qin, C Hu, L Lin, X Feng *J. Am. Chem. Soc.* **133** 15268 (2011)
163. Y Cai, X Liu, J Jiang, W Chen, L Lin, X Feng *J. Am. Chem. Soc.* **133** 5636 (2011)
164. L Zhou, L Lin, J Ji, M Xie, X Liu, X Feng *Org. Lett.* **13** 3056 (2011)
165. C-S Da, J-R Wang, X-G Yin, X-Y Fan, Y Liu, S-L Yu *Org. Lett.* **11** 5578 (2009)
166. J Y Lee, Y S You, S H Kang *J. Am. Chem. Soc.* **133** 1772 (2011)
167. S Padilla, R Tejero, J Adrio, J C Carretero *Org. Lett.* **12** 5608 (2010)
168. H Xu, C Wolf *Synlett* 2765 (2010)
169. H-L Teng, F-L Luo, H-Y Tao, C-J Wang *Org. Lett.* **13** 5600 (2011)
170. S K Ray, P K Singh, V K Singh *Org. Lett.* **13** 5812 (2011)
171. M Shigeno, T Yamamoto, M Murakami *Chem. – Eur. J.* **15** 12929 (2009)
172. D E Kim, V Ratovelomanana-Vidal, N Jeong *Adv. Synth. Catal.* **352** 2032 (2010)
173. C Shao, H-J Yu, N-Y Wu, P Tian, R Wang, C-G Feng, G-Q Lin *Org. Lett.* **13** 788 (2011)
174. Z Cui, H-J Yu, R-F Yang, W-Y Gao, C-G Feng, G-Q Lin *J. Am. Chem. Soc.* **133** 12394 (2011)
175. E G Gutierrez, C J Wong, A H Sahin, A K Franz *Org. Lett.* **13** 5754 (2011)
176. C-D Hwang, D-R Hwang, B-J Uang *J. Org. Chem.* **63** 6762 (1998)
177. K Mikami, M Terada, T Nakai *J. Am. Chem. Soc.* **112** 3949 (1990)
178. Z Yang, Z Wang, S Bai, K Shen, D Chen, X Liu, L Lin, X Feng *Chem. – Eur. J.* **16** 6632 (2010)
179. Z Yang, Z Wang, S Bai, X Liu, L Lin, X Feng *Org. Lett.* **13** 596 (2011)
180. S Oi, E Terada, K Ohuchi, T Kato, Y Tachibana, Y Inoue *J. Org. Chem.* **64** 8660 (1999)
181. K Zheng, C Yin, X Liu, L Lin, X Feng *Angew. Chem., Int. Ed.* **50** 2573 (2011)
182. Y Huang, E Tokunaga, S Suzuki, M Shiro, N Shibata *Org. Lett.* **12** 1136 (2010)
183. Y Xu, S Matsunaga, M Shibasaki *Org. Lett.* **12** 3246 (2010)
184. K Lang, J Park, S Hong *J. Org. Chem.* **75** 6424 (2010)
185. M-W Chen, Y Duan, Q-A Chen, D-S Wang, C-B Yu, Y-G Zhou *Org. Lett.* **12** 5075 (2010)
186. M Uehara, H Suematsu, Y Yasutomi, T Katsuki *J. Am. Chem. Soc.* **133** 170 (2011)
187. J-F Zhao, B-H Tan, M K Zhu, T-B W Tjan, T-P Loh *Adv. Synth. Catal.* **352** 2085 (2010)
188. J-F Zhao, T-B W Tjan, B-H Tan, T-P Loh *Org. Lett.* **11** 5714 (2009)
189. C Sui-Seng, F Freutel, A J Lough, R H Morris *Angew. Chem., Int. Ed.* **47** 940 (2008)
190. W Li, X Sun, L Zhou, G Hou, S Yu, X Zhang *J. Org. Chem.* **74** 1397 (2009)
191. C Benhaim, L Bouchard, G Pelletier, J Sellstedt, L Kristofova, S Daigneault *Org. Lett.* **12** 2008 (2010)
192. D Xiong, M Wu, S Wang, F Li, C Xia, W Sun *Tetrahedron: Asymmetry* **21** 374 (2010)
193. M Braun, M Sigloch, J Cremer *Adv. Synth. Catal.* **349** 337 (2007)
194. S Eagon, J Kim, K Yan, D Haddenham, B Singaram *Tetrahedron Lett.* **48** 9025 (2007)
195. X Zhou, X Liu, X Yang, D Shang, J Xin, X Feng *Angew. Chem., Int. Ed.* **47** 392 (2008)
196. K Matsumoto, T Yamaguchi, T Katsuki *Chem. Commun.* 1704 (2008)
197. K Suyama, Y Sakai, K Matsumoto, B Saito, T Katsuki *Angew. Chem., Int. Ed.* **49** 797 (2010)
198. J Fujisaki, Ken Matsumoto, Kaz Matsumoto, T Katsuki *J. Am. Chem. Soc.* **133** 56 (2011)
199. J-M Brunel, O Legrand, G Buono *Tetrahedron: Asymmetry* **10** 1979 (1999)
200. F Yang, D Zhao, J Lan, P Xi, L Yang, S Xiang, J You *Angew. Chem., Int. Ed.* **47** 5646 (2008)
201. T Ukon, T Harada *Eur. J. Org. Chem.* 4405 (2008)
202. M North, M Omedes-Pujol *Tetrahedron Lett.* **50** 4452 (2009)
203. G Xia, H Yamamoto *J. Am. Chem. Soc.* **128** 2554 (2006)
204. G Zhang, E Yashima, W-D Woggon *Adv. Synth. Catal.* **351** 1255 (2009)
205. M Rachwalski, S Lésniak, E Sznajder, P Kiełbasiński *Tetrahedron: Asymmetry* **20** 1547 (2009)
206. K Ito, S Eno, B Saito, T Katsuki *Tetrahedron Lett.* **46** 3981 (2005)
207. X-B Wang, K Kodama, T Hirose, X-F Yang, G-Y Zhang *Tetrahedron: Asymmetry* **21** 75 (2010)
208. Y Wang, D Liu, Q Meng, W Zhang *Tetrahedron: Asymmetry* **20** 2510 (2009)
209. J-i Ito, S Ujiie, H Nishiyama *Chem. – Eur. J.* **16** 4986 (2010)
210. C Hedberg, K Killstrlm, P Brandt, L K Hansen, P G Andersson *J. Am. Chem. Soc.* **128** 2995 (2006)
211. P Cheruku, A Paptchikhine, M Ali, J-M Neudörf, P G Anderssonl *Org. Biomol. Chem.* **6** 366 (2008)
212. M Schönleber, R Hilgraf, A Pfaltz *Adv. Synth. Catal.* **350** 2033 (2008).
213. W-J Lu, Y-W Chen, X-L Hou *Adv. Synth. Catal.* **352** 103 (2010)
214. J J Verendel, T Zhou, J-Q Li, A Paptchikhine, O Lebedev, P G Andersson *J. Am. Chem. Soc.* **132** 8880 (2010)
215. A Baeza, A Pfaltz *Chem. – Eur. J.* **16** 2036 (2010)
216. J-Q Li, A Paptchikhine, T Govender, P G Andersson *Tetrahedron: Asymmetry* **21** 1328 (2010)

217. T Irrgang, D Friedrich, R Kempe *Angew. Chem., Int. Ed.* **50** 2183 (2011)
218. D T Cohen, B Cardinal-David, K A Scheidt *Angew. Chem., Int. Ed.* **50** 1678 (2011)
219. C-T Chen, J-Q Kao, S B Salunke, Y-H Lin *Org. Lett.* **13** 26 (2011)
220. Y Wu, F Mao, F Meng, X Li *Adv. Synth. Catal.* **353** 1707 (2011)
221. H Y Kim, K Oh *Org. Lett.* **13** 1306 (2011)
222. S Ge, J F Hartwig *J. Am. Chem. Soc.* **133** 16330 (2011)
223. J M O'Brien, K-s Lee, A H Hoveyda *J. Am. Chem. Soc.* **132** 10630 (2010)
224. A Guzman-Martinez, A H Hoveyda *J. Am. Chem. Soc.* **132** 10634 (2010)
225. J F Teichert, S Zhang, A W van Zijl, J W Slaa, A J Minnaard, B L Feringa *Org. Lett.* **12** 4658 (2010)
226. C-J Hou, W-L Guo, X-P Hu, J Deng, Z Zheng *Tetrahedron: Asymmetry* **22** 195 (2011)
227. C Solé, A Whiting, H Gulyás, E Fernández *Adv. Synth. Catal.* **353** 376 (2011)
228. C Zhang, S-B Yu, X-P Hu, D-Y Wang, Z Zheng *Org. Lett.* **12** 5542 (2010)
229. J F Teichert, B L Feringa *Chem. Commun.* **47** 2679 (2011)
230. J Wencel-Delord, A Alexakis, C Crévisy, M Mauduit *Org. Lett.* **12** 4335 (2010)
231. B M Trost, B R Taft, J T Masters, J-P Lumb *J. Am. Chem. Soc.* **133** 8502 (2011)
232. Z-Y Xue, Q-H Li, H-Y Tao, C-J Wang *J. Am. Chem. Soc.* **133** 11757 (2011)
233. A Chougnet, G Zhang, K Liu, D Häussinger, A Kägi, T Allmendinger, W-D Woggon *Adv. Synth. Catal.* **353** 1797 (2011)
234. D Cartigny, K Püntener, T Ayad, M Scalone, V Ratovelomanana-Vidal *Org. Lett.* **12** 3788 (2010)
235. N Pannetier, J-B Sortais, J-T Issenhuth, L Barloy, C Sirlin, A Holuigue, L Lefort, L Panella, J G de Vries, M Pfeffer *Adv. Synth. Catal.* **353** 2844 (2011)
236. C Lu, Z Luo, L Huang, X Li *Tetrahedron: Asymmetry* **22** 722 (2011)
237. N Kurono, T Yoshikawa, M Yamasaki, T Ohkuma *Org. Lett.* **13** 1254 (2011)
238. H Geng, X Zhang, M Chang, L Zhou, W Wu, X Zhang *Adv. Synth. Catal.* **353** 3039 (2011)
239. J Qin, F Chen, Z Ding, Y-M He, L Xu, Q-H Fan *Org. Lett.* **13** 6568 (2011)
240. T Wang, L-G Zhuo, Z Li, F Chen, Z Ding, Y He, Q-H Fan, J Xiang, Z-X Yu, A S C Chan *J. Am. Chem. Soc.* **133** 9878 (2011)
241. F Chen, Z Ding, J Qin, T Wang, Y He, Q-H Fan *Org. Lett.* **13** 4348 (2011)
242. R Soni, J-M Collinson, G C Clarkson, M Wills *Org. Lett.* **13** 4304 (2011)
243. R Shintani, T Hayashi *Org. Lett.* **13** 350 (2011)
244. S Kang, J Han, E S Lee, E B Choi, H-K Lee *Org. Lett.* **12** 4184 (2010)
245. X-M Zhou, J-D Huang, L-B Luo, C-L Zhang, Z Zheng, X-P Hu *Tetrahedron: Asymmetry* **21** 420 (2010)
246. S A Lee, S H Kwak, K-I Lee *Chem. Commun.* **47** 2372 (2011)
247. R Shintani, Y-T Soh, T Hayashi *Org. Lett.* **12** 4106 (2010)
248. Xia Zhang, B Cao, S Yu, Xum Zhang *Angew. Chem., Int. Ed.* **49** 4047 (2010)
249. T Pullmann, B Engendahl, Z Zhang, M Hölscher, A Zanotti-Gerosa, A Dyke, G Franciò, W Leitner *Chem. – Eur. J.* **16** 7517 (2010)
250. H Fernández-Pérez, S M A Donald, I J Munslow, J Benet-Buchholz, F Maseras, A Vidal-Ferran *Chem. – Eur. J.* **16** 6495 (2010)
251. H Landert, F Spindler, A Wyss, H-U Blaser, B Pugin, Y Ribourduoille, B Gschwend, B Ramalingam, A Pfaltz *Angew. Chem., Int. Ed.* **49** 6873 (2010)
252. W Tang, A G Capacci, A White, S Ma, S Rodriguez, B Qu, J Savoie, N D Patel, X Wei, N Haddad, N Grinberg, N K Yee, D Krishnamurthy, C H Senanayake *Org. Lett.* **12** 1104 (2010)
253. X Feng, Y Wang, B Wei, J Yang, H Du *Org. Lett.* **13** 3300 (2011)
254. T Nishimura, Y Maeda, T Hayashi *Org. Lett.* **13** 3674 (2011)
255. M A Chávez, S Vargas, A Suárez, E Álvarez, A Pizzano *Adv. Synth. Catal.* **353** 2775 (2011)
256. T Thaler, L-N Guo, A K Steib, M Raducan, K Karaghiosoff, P Mayer, P Knochel *Org. Lett.* **13** 3182 (2011)
257. Y Zhao, H Huang, J Shao, C Xia *Tetrahedron: Asymmetry* **22** 769 (2011)
258. G S Mahadik, S R Hitchcock *Tetrahedron: Asymmetry* **21** 33 (2010)
259. J Streuff, D E White, S C Virgil, B M Stoltz *Nat. Chem.* **3** 192 (2010)
260. Y Huang, R J Chew, Y Li, S A Pullarkat, P-H Leung *Org. Lett.* **13** 5862 (2011)
261. R I McDonald, P B White, A B Weinstein, C P Tam, S S Stahl *Org. Lett.* **13** 2830 (2011)
262. Z Cao, Y Liu, Z Liu, X Feng, M Zhuang, H Du *Org. Lett.* **13** 2164 (2011)
263. K Kikushima, J C Holder, M Gatti, B M Stoltz *J. Am. Chem. Soc.* **133** 6902 (2011)
264. Y Wang, M J P Vaismaa, A M Hämäläinen, J E Tois, R Franzén *Tetrahedron: Asymmetry* **22** 524 (2011)
265. Q-Y Zhao, Z-L Yuan, M Shi *Adv. Synth. Catal.* **353** 637 (2011)
266. S J Kim, D O Jang *J. Am. Chem. Soc.* **132** 12168 (2010)
267. K A Nolin, R W Ahn, Y Kobayashi, J J Kennedy-Smith, F D Toste *Chem. – Eur. J.* **16** 9555 (2010)
268. X Gao, H Han, M J Krische *J. Am. Chem. Soc.* **133** 12795 (2011)
269. O Soltani, M A Ariger, H Vázquez-Villa, E M Carreira *Org. Lett.* **12** 2893 (2010)
270. L Mantilli, C Mazet *Chem. Commun.* **46** 445 (2010)
271. Y Zhou, J Dong, F Zhang, Y Gong *J. Org. Chem.* **76** 588 (2011)
272. Y Tanaka, M Kanai, M Shibasaki *J. Am. Chem. Soc.* **132** 8862 (2010)
273. S Li, S-F Zhu, J-H Xie, S Song, C-M Zhang, Q-L Zhou *J. Am. Chem. Soc.* **132** 1172 (2010)
274. S B Han, H Han, M J Krische *J. Am. Chem. Soc.* **132** 1760 (2010)
275. P Kaur, S Pindi, W Wever, T Rajale, G Li *J. Org. Chem.* **75** 5144 (2010)
276. Y Li, K Ding, C A Sandoval *Org. Lett.* **11** 907 (2009)
277. Y Yasutomi, H Suematsu, T Katsuki *J. Am. Chem. Soc.* **132** 4510 (2010)
278. F Guo, G Lai, S Xiong, S Wang, Z Wang, Y Yasutomi, H Suematsu, T Katsuki *Chem. – Eur. J.* **16** 6438 (2010)
279. Z-Y Xue, T-L Liu, Z Lu, H Huang, H-Y Tao, C-J Wang *Chem. Commun.* **46**. 1727 (2010)
280. T Arai, N Yokoyama, H Mishiro, H Sato *Angew. Chem., Int. Ed.* **49** 7895 (2010)
281. T Miura, M Morimoto, M Murakami *J. Am. Chem. Soc.* **132** 15836 (2010)
282. S B Han, X Gao, M J Krische *J. Am. Chem. Soc.* **132** 9153 (2010)
283. T Imamoto, K Tamura, Z Zhang, Y Horiuchi, M Sugiya, K Yoshida, A Yanagisawa, I D Gridnev *J. Am. Chem. Soc.* **134** 1754 (2012)

[a] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*