Review

Chiral Monophosphines as Ligands for Asymmetric Organometallic Catalysis#

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Chelating chiral diphosphines are often used as ligands of organometallic complexes. However monophosphines, or more generally ligands with one phosphorus linked to one or several heteroatom, may also be useful. This review gives the main results obtained in that area, by considering the classes of monodentate chiral ligands bearing one P(III) atom and involved in asymmetric catalysis with organometallic complexes.

Key words chiral monophosphines; organometallic catalysis; enantioselectivity; monodentate ligand

1. Introduction

The usefulness of triphenylphosphine as ligand of rhodium or ruthenium for the elaboration of complexes active in homogeneous catalysis was pioneered by Wilkinson *et al*.[2)] This gave later a basis for the elaboration of asymmetric catalysts. Homogeneous asymmetric hydrogenation started with modest results (ee<15%) in 1968 using chiral monophosphine **1a** (mppp) (Fig. 1) as ligand.[3,4)] Neomenthyldiphenylphosphine **6** (nmdpp) and menthyldiphenylphosphine **7** (mdpp) were prepared in 1971 by Morrison *et al*,[5)] giving up to 61% ee in some cases. Knowles *et al*. also published in 1972 some interesting results (ee<90%) with chiral phosphines **2a** (pamp) and **4** (camp).[6)] At the same time alkyldimenthylphosphines **10** were used by Wilke, Bogdanovic *et al*. as ligand of nickel complexes in the catalysis of alkene codimerization and alkene-1,3-dienes codimerization.[7,8)]

In 1971—1972 we demonstrated that a chelating chiral C_2-symmetric diphosphine (diop) without asymmetric phosphorus atoms was an excellent enantioselective catalyst (ee <88%).[9,10)] Since that time C_2-symmetric diphosphines have been widely and successfully investigated, releasing chiral monophosphines in the darkness. A multitude of chelating diphosphines are presently known (of C_1 or C_2-symmetry), some of them are patented because of industrial applications. This area has been often reviewed since the early developments, see for example in chronological order refs.[11—17)]

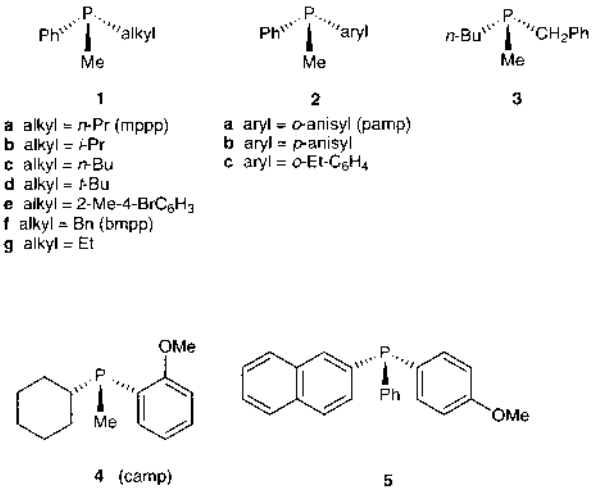

Fig. 1. List of Phosphines Where Phosphorus is the Sole Source of Chirality

By contrast to chiral diphosphines, the field of chiral monophosphines remained stagnant for a long time. However there were in literature some indications that more consideration should be given to this family of compounds, as outlined in the following section.

2. Potential Interest of Chiral Monophosphines in Asymmetric Catalysis

It is obvious that chelating diphosphines are especially well fitted for catalytic species involving a transition metal bond to two phosphorus (at least in the stereodetermining step). This condition is fulfilled with the Wilkinson catalyst for hydrogenation. Of course monophosphines may also play a useful role, if two equivalents of phosphines are available for the metallic center, although a cis-trans mixture of complexes may be generated on square planar systems.[20)]

One also may expect a specific use of monophosphines when the catalytic complexes only accomodate one phosphine or if a monodentate ligand is required for the generation of a catalytically active species.

Monophosphines, and more generally phosphorus derivatives where phosphorus is connected to one or several heteroatoms, may be of interest in asymmetric catalysis, even in the absence of chelate effects. In this review we shall only consider monodentate phosphine ligands. The case involving chelation by an additional heteroatom such as nitrogen has already been reviewed.[22)]

3. Structural Classification of Chiral Monophosphines and Analogues

The phosphorus ligands may be classified according to the nature of the substituents attached to the phosphorus atom. The usual case is that of *phosphines*, where there are three P–C bonds. The main chiral monophosphines of potential interest for asymmetric catalysis are listed in Figs. 1—4. In Fig. 1 are placed the phosphines having an asymmetric phosphorus center as sole source of chirality. The monophosphines involving a chiral unit connected to phosphorus (which may be or not a stereogenic center) are in Figs. 2, 3. In Fig. 4 are indicated some examples of phosphines with axial or planar chirality.

Phosphinites, *phosphonites*, *phosphites*, *phosphinamides* and *phosphinimides* are phosphorus compounds with at least one P–O or P–N single bond. These compounds are outside

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# Dedicated to Professor Günther Wulff for his 65th birthday.

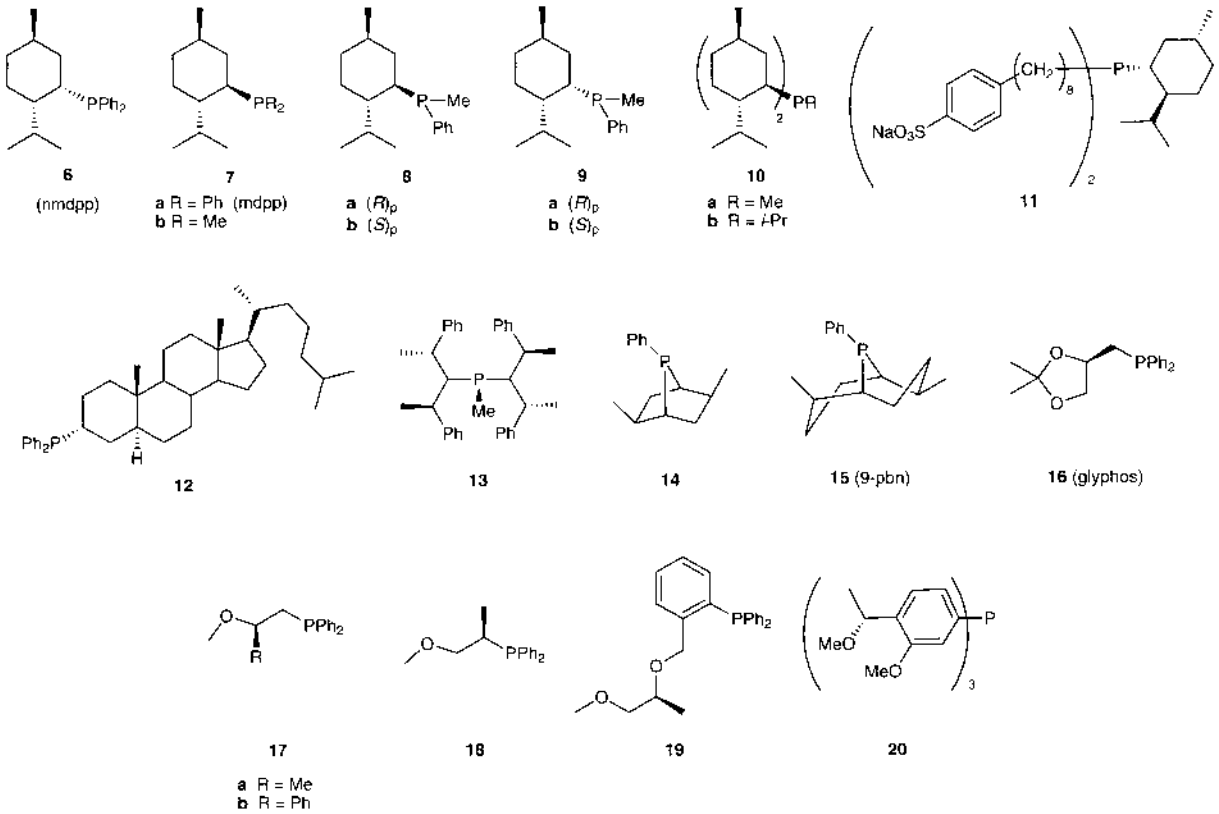

Fig. 2. List of Phosphines with Asymmetric Centers

of the scope of the present article, and will be reviewed elsewhere.[23)]

The preparation of various classes of phosphines will not be detailed here. The general approaches are the resolution of phosphine oxides by a chiral acid such as tartaric acid. Asymmetric syntheses of phosphines (asymmetric at P) from chiral phosphinates by nucleophilic displacement are very efficient.[24)] Enantiopure phosphinates are easily obtained from chiral oxazaphospholidines or oxathiaphospholidines.[25,26)] The preparation of phosphorus ligands where phosphorus is not a stereogenic center does not present difficulty. One widely used reaction is the nucleophilic displacement of a halide or tosylate by a phosphide such as $LiPPh_2$.

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Franz Lagasse was born in Boulogne Billancourt (France) in 1970. He received his diploma of organic chemistry in 1996. He studied the use of chiral acetals and aminals in asymmetric synthesis under the supervision of Prof. A. Alexakis from University of Pierre et Marie Curie (France). In 1997, he worked at the Research Institute of the pharmaceutical compagny Servier. Then, he joined the group of Prof. H. B. Kagan. His PhD thesis is focused on the synthesis of new ligands for organometallic asymmetric catalysis.

4. Use of Chiral Monophosphines in Asymmetric Organometallic Catalysis

4.1. Asymmetric Hydrogenation. Hydrogenation of C=C Double Bonds The first examples of asymmetric hydrogenation were simultaneously described in 1968 by Horner *et al*.[3] and Knowles *et al*.[4] The rhodium complexes were prepared *in situ* from $[Rh(1,5\text{-hexadiene})Cl]_2$ by addition of two equivalents (by respect to rhodium) of phosphine **1a** or from $RhCl_3L_3$ (L=**1a**) by treatment with hydrogen (20 atm) in the presence of NEt_3. The reduction of some styrene derivatives gave ee's not higher than 20% (Fig. 5). The study of the family of phosphines **1a**—**1e** showed that **1b** provided the highest ee (19% ee).[3b] 2-Methoxystyrene also gave low ee's (<15%) in asymmetric hydrogenation using ligands **1a**, **1b**.[3b] Morrison *et al*. studied in 1971 rhodium catalysts involving neomenthyl- or menthyldiphenylphosphines **6** and **7a**, some results for hydrogenation of conjugated acids **37** are indicated in Fig. 5.[5a] In 1972 it was shown that some phosphines with an asymmetric phosphorus may lead to high enantioselectivities in hydrogenation when one of the groups connected to phosphorus is an *ortho*-anisyl ring.[27] Various α-acylaminoacrylic acids **39**, **41** were transformed into *N*-acylaminoacids (**40**, **42**) with ee's up to 90%. Some examples are given in Fig. 5. The rhodium catalyst was prepared in smooth conditions from $[Rh(1,5\text{-hexadiene})Cl]_2$ or in more severe conditions from $RhCl_3{,}3H_2O$ and addition of two equivalents of chiral ligands. The authors established that two monophosphines L* are needed for one rhodium. The monoligand complex gave slow hydrogenation and low ee, addition *in situ* of another equivalent of ligand gave high ee and fast rates. Addition of one equivalent of Me_2PhP to the monoligand complex gave fast rates but only one half of the ee. Finally isolation of crystalline $[Rh(cod)Cl(\mathbf{2a})_2]$ and $[Rh(cod)(\mathbf{2a})_2]^+$ $(C_6H_5)_4B^-$ is also a nice confirmation of the 1 : 2 stoichiometry for the Rh/L* complex. The asymmetric hydrogenation of *N*-acetyldehydrophenylalanine **41** (R^1=Me) has been studied in great details with the rhodium/camp **4** complex. The replacement of the *ortho*-anisyl group in camp **4** by a 2-Me-4-Br-C_6H_3 group (**1e**) decreased only moderately the enantioselectivity. The methoxy group is then useful mainly for steric reasons, and does not act as a permanent chelating group (see a recent report of Imamoto *et al*. on the influence of the *ortho*-anisyl group in asymmetric hydrogenation[27]). A conjugated ketone, piperitenone **45** (Fig. 5), has been hydrogenated to pulegone (ee<38%) as the major product.[28a] The catalyst was $[Rh(cod)(camp)_2]^+BF_4$- and the reaction was performed in DMF or methanol.

Diastereomeric P-chiral phosphines involving a menthyl or neomenthyl fragment (**8**, **9**) were used in Hoffman-La Roche to prepare rhodium catalysts for hydrogenation.[29] For example Geranic acid (with nmdpp **6**) and *N*-acetyl 6-methyl-dehydrotryptophane (with **9b**) led to products of ee's up to 70% and 37% respectively.

Ferrocenylphosphine **31** gave a quite active and enantioselective rhodium catalyst for asymmetric hydrogenation of *N*-acetyldehydrophenylalanine (87% ee).[30] It has not been established if the ligand (2 equiv. by respect to Rh) acts as monodentate or if one of the oxygens of the vicinal cyclic acetal interacts with rhodium.

Monophosphines where the phosphorus atom is part of a saturated ring have been investigated recently in asymmetric hydrogenation.

The *trans*-2,5-dimethyl-1-phenylphospholane **23a** provided 60% ee in the Rh-catalyzed hydrogenation of the methyl ester of *N*-acetyl-dehydrophenylalanine and 65% ee in the reduction of dimethyl itaconate.[31] Improved enantioselectivity (*N*-acetyl phenylalanine of 82% ee) was obtained with the *trans*-1,2,5-triphenyl analog **23b**.[32a] A careful control of experimental conditions allowed even to reach 92% ee.[32b] Phosphiranes **21a** and **21b** have been used to prepare the corresponding cationic rhodium complexes. X-ray crystallography of $[Rh(cod)(\mathbf{21a})2]^+$ PF_6^- showed a significant deviation from the square planar coordination around rhodium, due to steric interactions between the two ligands in *cis* relationship.[33] Hydrogenation of *N*-acetyl dehydrophenylalanine **41** (R=Me) provided up to 76% ee (see Fig. 5). The authors did not eliminate the possibility that the actual catalyst involved a phosphine deriving from the phosphiranes by an *in situ* hydrogenolytic ring opening. Itaconic acid was hydrogenated into 2-methyl succinic acid (26% ee) in the presence of a rhodium complex containing **21b** as ligand. The phosphetanes **22** were also checked as ligand of rhodium or iridium in asymmetric hydrogenation.[34] Phosphetane **22b** is a poor ligand for rhodium and gave 40% ee in the hydrogenation of the methyl ester of *N*-acetyldehydrophenylalanine.

Hydrogenation of C=O Double Bonds Camp **4** was screened in 1975 at Monsanto as ligand of rhodium catalysts for hydrogenation of ketones.[28b] Methyl acetylacetate has been transformed into methyl β-hydroxybutyrate with 71% ee. Complex $[Rh(nbd)(\mathbf{1f})_2]^+$ ClO_4^- has a low catalytic activity at room temperature under 1 atm hydrogen for hydrogenation of acetophenone (8% ee) and butan-2-one (2% ee).[35] Negligible ee's (<1%) were given by catalyst $[Rh(nbd)(\mathbf{1g})_2]^+$ PF_6^- in hydrogenation of the same ketones.[36]

One carbonyl group of a cyclopentanetrione has been reduced into an α-ketol which is an intermediate of total synthesis of prostaglandin E_1 in the presence of a Rh/camp catalyst.[37] Unfortunately the enantioselectivity is low, the product (68% ee) was recovered after crystallization.

Since the early time of asymmetric hydrogenation there were no major improvements in enantioselectivities using rhodium/monophosphine complexes in the asymmetric hydrogenation of C=C or C=O double bonds. However 1,2,5-triphenylphospholane **23b** has been found recently to catalyze asymmetric hydrogenation of **41** with the same level of enantioselectivity than camp.[32] This leaves good hope that a suitable tuning of the structure of phospholanes will lead to excellent ligands for asymmetric hydrogenation.

4.2. Alkene Codimerization and Related Processes Asymmetric codimerization of olefins or conjugated dienes was quite successful already in the early seventies. Wilke, Bogdanovic *et al*. developed the use of a family of chiral nickel complexes with one equivalent of alkyldimenthylphosphines **10** by respect to nickel.[7,8,38] The chemistry which was developed at the Max–Planck-Institut in Mülheim in early seventies used alkyl phosphines prepared from terpenes. Some examples of reaction are listed in Fig. 6. The phosphine giving the highest enantioselectivity was dimenthyl isopropyl phosphine **10b**. *Exo*-2-vinylnorbornane (80% ee) and *exo*-2-vinylnorbornene (77% ee) were obtained for reactions performed at −97 °C and −65 °C respectively (Fig. 6). A crystalline complex formed from methyl(π-1-methyl-2-

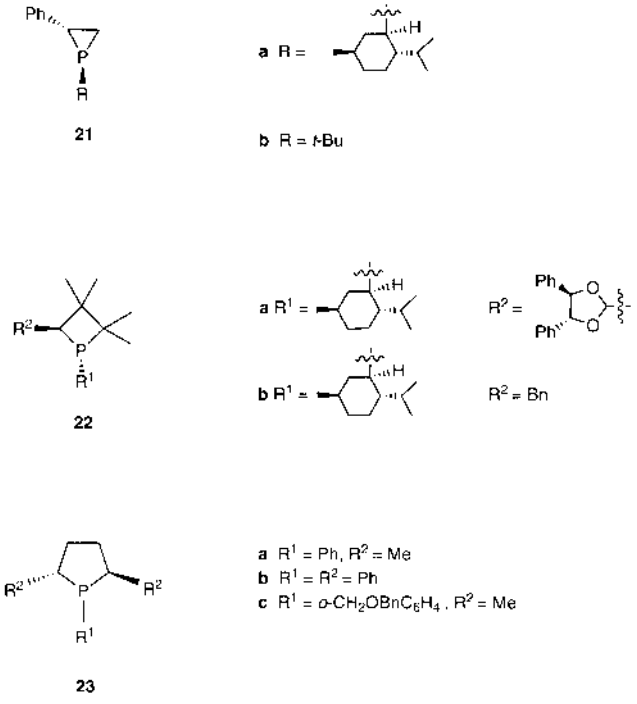

Fig. 3. List of Phosphines Included in a Ring with Asymmetric Centers

butenyl)nickel and (−)-dimenthyl methyl phosphine **10a**. The X-ray crystallographic structure showed a square planar coordination with **10a** coordinated to Ni, the isopropyl group of one menthyl being located close to the nickel above the coordination plane. The authors assumed that the catalytic cycle involves a square planar hydride nickel complex, with the alkene coordinated *cis* to the hydride and *trans* to the phosphine. This later introduces a steric control in the insertion reaction and gives the asymmetric induction.

RajanBabu *et al*. reinvestigated hydrovinylation reactions with nickel catalysts.[39] They found a synergistic effect between counteranions and hemilabile coordination of a chiral monophosphine. Both yields and ee's were highly dependent of the suitable combination of these parameters. The authors selected mop **25a** and analogues as the chiral monophosphines. Mop has been previously devised by Hayashi *et al*.[40] Some results (ee's up to 80%) are indicated in Fig. 6. Phospholanes **23** also led to some asymmetric induction (ee's up to 50%) in the hydrovinylation of styrene (Fig. 6).[39]

An interesting intramolecular C–H/olefins coupling in a 1,5-diene has been described by Murai *et al*., with a catalyst $[RhCl(cyclooctene)_2]_2$/L* where L* is the ferrocenylphosphine **30**.[41] Some details are given in Fig. 7. The reaction was strongly inhibited by bidentate diphosphines.

4.3. Allylic Substitution Hayashi *et al*. pioneered the

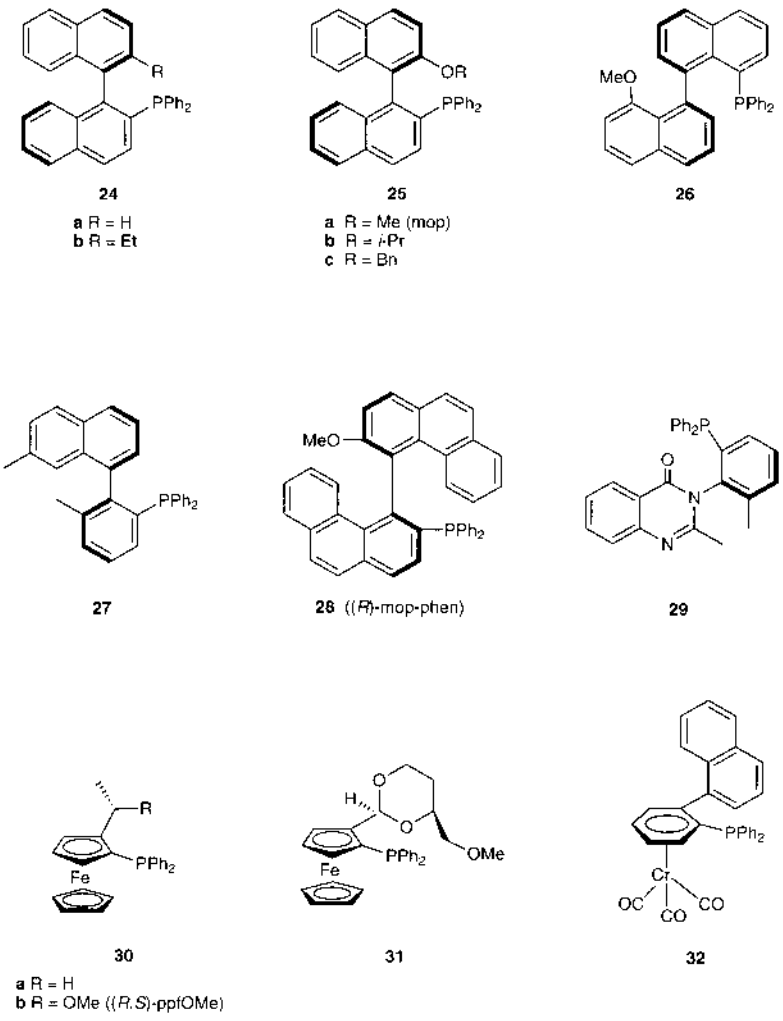

Fig. 4. List of Phosphines with Axial or Planar Chirality

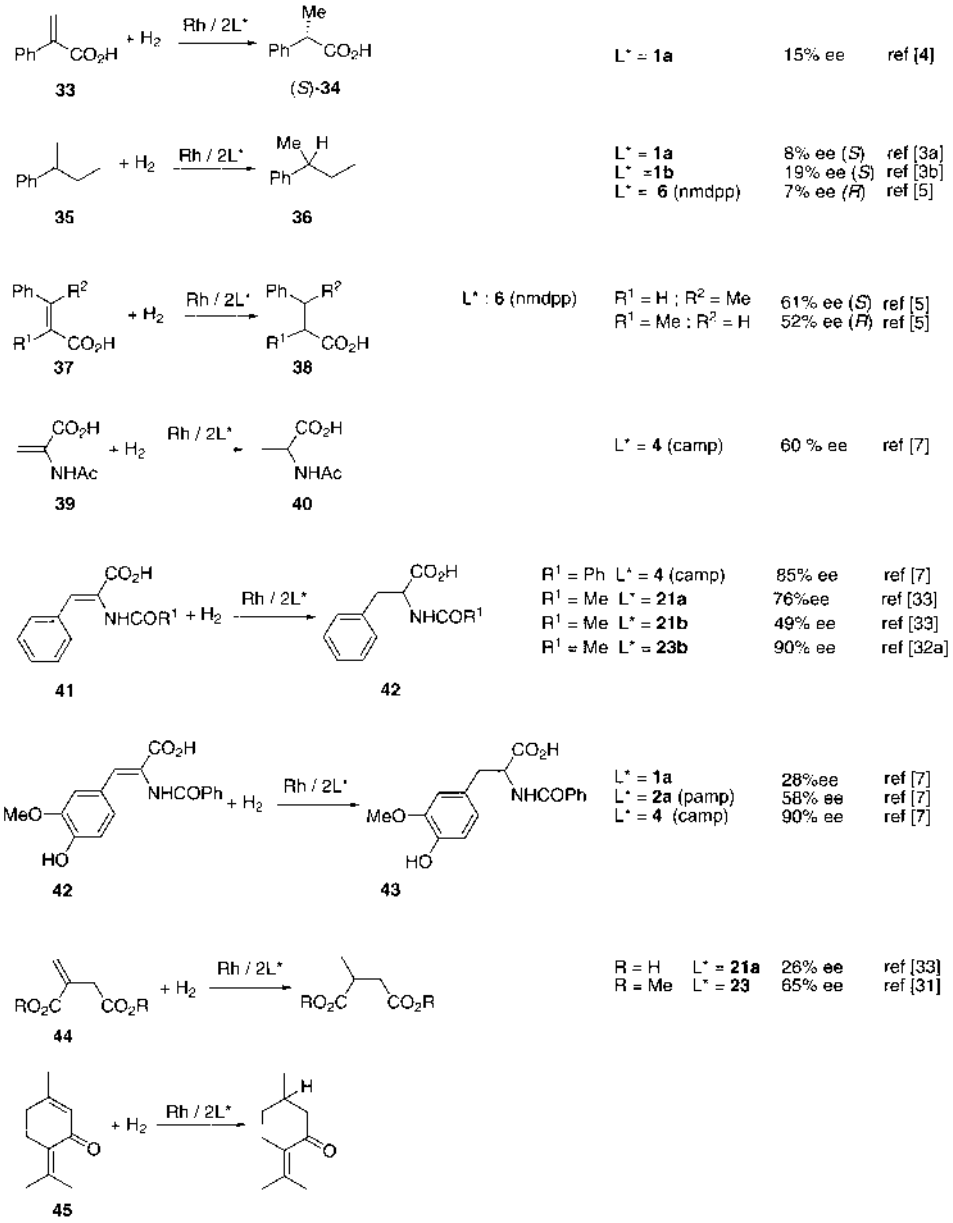

Fig. 5. Asymmetric Hydrogenation Reactions

use of chiral monophosphines. They prepared a large variety of 2-(diphenylphosphino)-2′-alkoxy-1,1′-binaphthyls (mops **25**)[40a] as well as 1-[2-(diphenylphosphino)-ferrocenyl]alkyl methyl ether ppfOMe **30b**.[40b] Palladium-mop complexes were useful in catalytic asymmetric reduction of allylic esters with formic acid.[42] Excellent yields and ee's (up to 85%) were obtained at room temperature with 1% catalyst (Fig. 8). The phenanthrene analog **28** of mop is also efficient. By contrast reduction is very slow and not regioselective with chelating diphosphines as binap. The reaction involves a π-allylpalladium intermediate. The X-ray crystal structure of [PdCl(η^3-1,1-dimethylallyl)mop] showed that the naphthyl ring substituted with a methoxy group lies above palladium, the methoxy group being not coordinated to the metal. However the monodentate character of mop **25a** has been recently questioned by Kocovsky *et al*.[43] These authors have been able to get the X-ray crystal structure of [(mop)Pd(η^3-C_3H_5)]$^+$ TfO^- where a η^2 coordination of the phosphine has been observed thanks to a P, C_σ ligation. The C-bonding involves C_1 position vicinal to the methoxy group. This unusual coordination could be of importance in some part of the catalytic cycle.

8-MeO-mop **26** has been recently synthesized by Fuji *et al*.[44] This new monodentate ligand provided excellent results in asymmetric reduction of allylic esters (Fig. 8).

The ferrocenylphosphine **31** bearing a cyclic acetal gave a moderate enantioselectivity in the allylic substitution on **46** (65% ee when benzylamine is the nucleophile).[30]

Fiaud *et al*. have studied the substitution reaction of cyclohex-2-enyl acetate with sodium dimethyl malonate or phenylzinc catalyzed by a palladium/phospholane **23b** complex.[45b] Unfortunately the product was only of 10% ee. Good results have been obtained by Marinetti *et al*. in the allylic substitution catalyzed by a palladium/phosphetane **22a** complex (Fig. 8).[46] A X-ray crystal structure of (η^3-C_3H_5)PdCl (**22a**) complex shows the monodentate character of the lig-

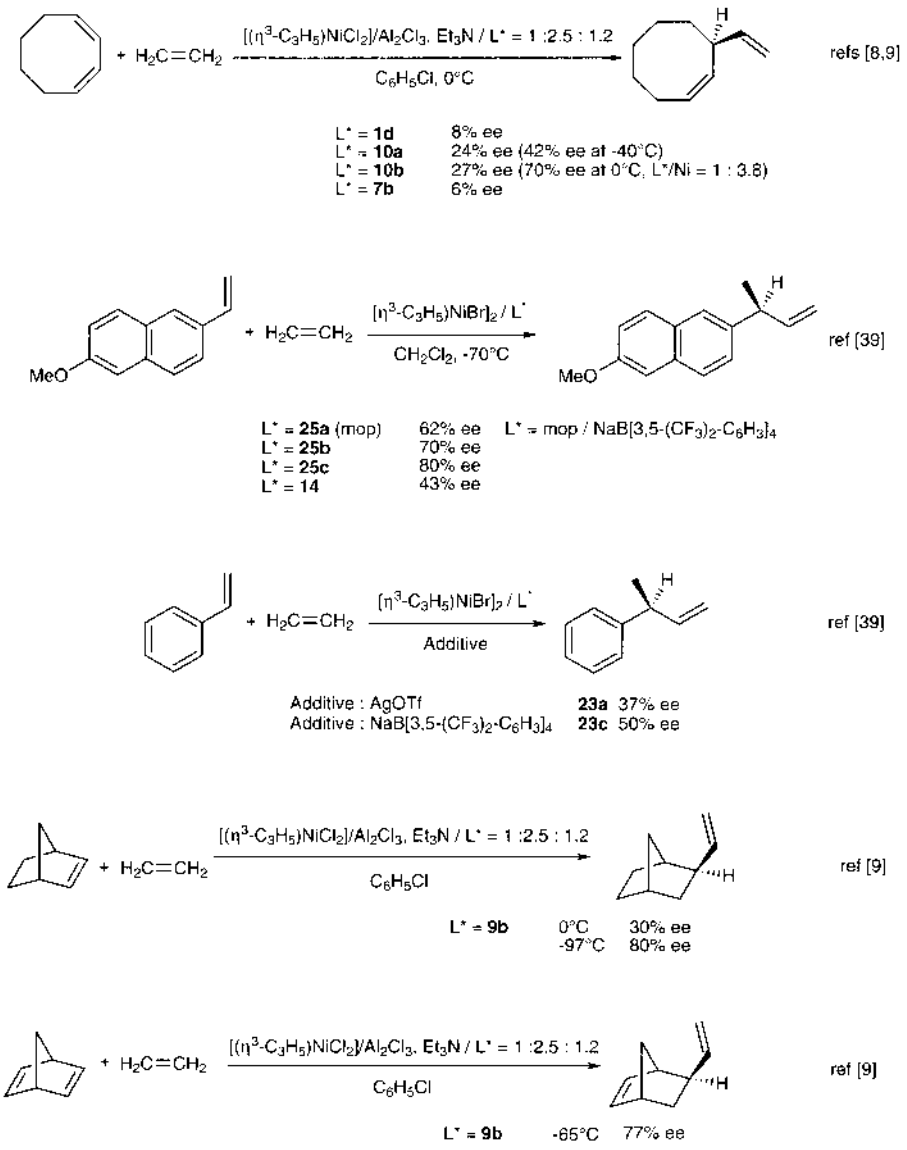

Fig. 6. Alkene Codimerization Reactions

and without coordination to Pd of one of its oxygens.

A new promissing chiral monophosphine with planar chirality **32** has been prepared by Nelson and Hifliker.[47] It gave a Pd(II) complex which catalyzed the alkylation of 1-phenylcinnamyl acetate **46** by the anion of dimethyl malonate (92% ee). The X-ray crystal structure of Pd(η^3-C_3H_5)(**32**)Br shows that the naphthyl ring shields the top side of the square planar Pd(II) metal.

The crowded trialkylphosphine **13** has been synthesized by Knochel *et al.*[48] The corresponding Pd(II) complex catalyzed the allylic alkylation of **46** by the anion of dimethyl malonate with 73% ee.

Some rigid chiral phosphines have been recently synthesized and are useful in palladium-catalyzed asymmetric allylic substitution. For example 9-pbn **15** gave 95% ee in the substitution reaction on **46** (Fig. 8).[49] This ligand is also very efficient (90—95% ee) in asymmetric substitution of **46** by various primary and secondary amines.[50] Monophosphine **14** with a rigid fused bicyclic [2.2.1] ring is excellent for asymmetric alkylation of **46** (Fig. 8).[51] A monodentate atropoisomeric quinazolinone phosphine ligand **29** has been screened in the allylic substitution on **46**, the product was obtained in 52% ee.[52] A propeller-shapped C_3-symmetric triaryl phosphine **20** is efficient in the palladium-catalyzed substitution of *O*-benzoyl-cyclopentene-3-ol by phtalimide, leading to a product of 82% ee.[53]

In conclusion many structural types of chiral monophosphines L* may generate enantioselective palladium catalysts of stoichiometry Pd/L*=1 : 2. A fine tuning of the structure of these ligands is possible and should give rise to useful developments.

The catalytic asymmetric reactions of π-allylpalladium complexes coordinated with achiral monophosphine has been recently reviewed.[54]

4.4. Cross-coupling Reactions Asymmetric C–C bond formation involving a Grignard cross-coupling has been widely studied by Hayashi and Kumada[40b] when the Grignard reagent derives from a secondary halide such as 1-phenylethylmagnesium chloride **47** (Fig. 9). The reagent stays in racemic composition because of its fast *in situ* racemisation compared to the reaction rate. The coupling reaction with vinyl bromide is catalyzed by the complex gener-

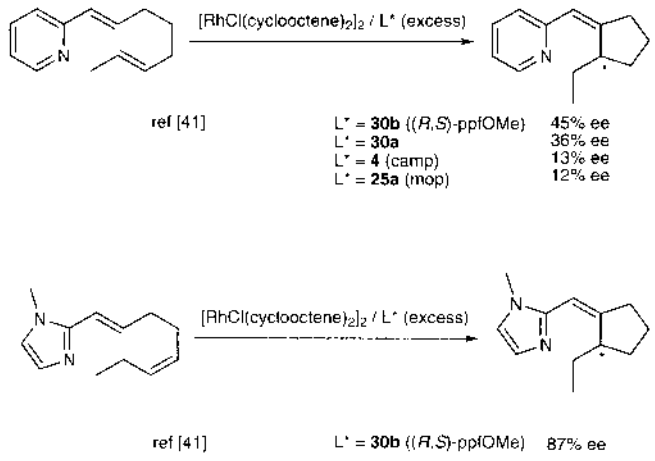

Fig. 7. Intramolecular C-H/Olefins Coupling Reactions

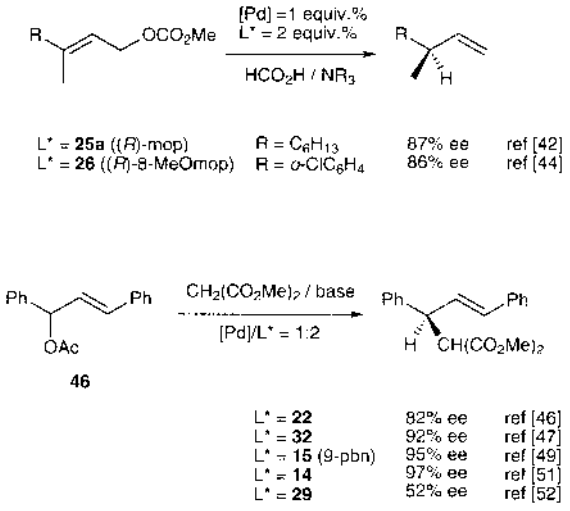

Fig. 8. Allylic Substitution Reactions

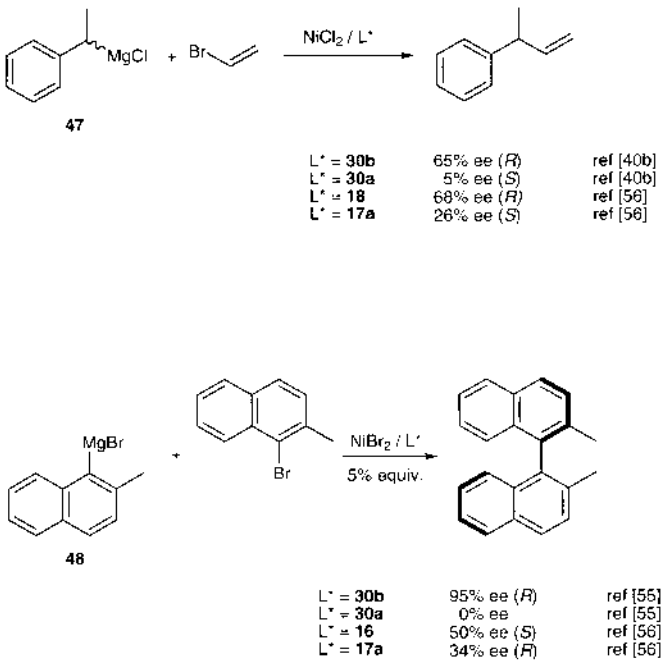

Fig. 9. Cross-Coupling Reactions

ated from $NiCl_2$ and various types of phosphines. High enantioselectivities were given by aminoferrocenylphosphines, however nitrogen which plays a key role for coordination with magnesium atom is not compulsory in order to observe some asymmetric induction (almost up to 60% ee, Fig. 9).

The C–C bond formation between two aryl systems may generate atropoisomerism. A new type of asymmetric catalysis has been developed by Hayashi *et al*. by reaction between an aromatic halide and an aromatic Grignard reagent (Fig. 8).[55] The catalyst was the combination between $NiCl_2$ and 3 equiv. of ferrocenylphosphine **30b** (ppfOMe). By this way 2,2′-dimethyl-1,1′-binaphthyl was produced with up to 95% ee (Fig. 9). The methoxy is essential for high enantioselectivity (phosphine **30a** gave a racemic product), presumably by acting as coordinating group to the Grignard reagent. Diphosphines were inefficient in this process. Several Nickel/alkoxy phosphines (**16**—**19**) catalysts have been investigated by Brunner *et al*. in the coupling reactions involving Grignard reagents **47** and **48**.[56] Some results are indicated in Fig. 9.

4.5. Hydroformylation Asymmetric hydroformylation and related processes developed mainly by the use of bidentate phosphorus ligands (review: ref. 57). The main problem is to combine a high enantioselectivity to a high regioselectivity. There are only a few examples involving a monodentate phosphine. Rhodium complexes with chiral ligands are frequently use. In the hydroformylation of styrene (Fig. 10) Nmdpp **1a** or bmpp **1f** have been reported to give some asymmetric induction (up to 20% ee) in hydroformylation of styrene.[58,59] By decreasing the temperature to 60 °C 50% ee could be reached with **1f**.[60] In the same reaction water-soluble phosphine **11** or dicol **12** provided negligible ee's[61,62] while a P-Phenylphosphepine (based on the 1,1′-binaphthyl skeleton) achieved 20% ee.[63] **1a** (mppp) has been studied at the BASF company.[64] A catalyst prepared from $[RhCl(cod)]_2$ and **1a** allowed to isolate hydratropaldehyde from styrene (at 200 bar) in 40% ee.

Asymmetric carboesterification usually gives higher enantioselectivity than the corresponding hydrocarbonylations. In Fig. 10 are indicated a few examples of carbomethoxycarbonylation in methanol catalyzed by the nmdp **6**/$Pd(dba)_2$ combination. Enantioselectivities up to 50% ee were reached.[65]

4.6. Hydrosilylation. Hydrosilylation of C=C Double Bonds In 1971—1972 were reported the first examples of asymmetric hydrosilylation of olefins in the presence of some platinum (II) complexes (Fig. 11).[66,67] The ligands were bmpp **1f**, nmdpp **6** and mdpp **7**, the enantiomeric excess of the product was not higher than 5%. Later palladium complexes afforded higher although moderate enantioselectivities, needing diphosphines as ligands. A breakthrough occured in 1991 with the introduction by Hayashi *et al*. in hydrosilylation of the chiral monophosphine mop **25a** as ligand of palladium catalysts.[68] Monodentate phosphine ligands generate a palladium catalyst which is more active than the similar complex with a diphosphine. The reason is the initial oxidative addition of the H–Si bond of $HSiCl_3$ on a Pd(0) center, which needs to be followed by an activation of olefin by coordination on an empty site. This cannot occurs in the

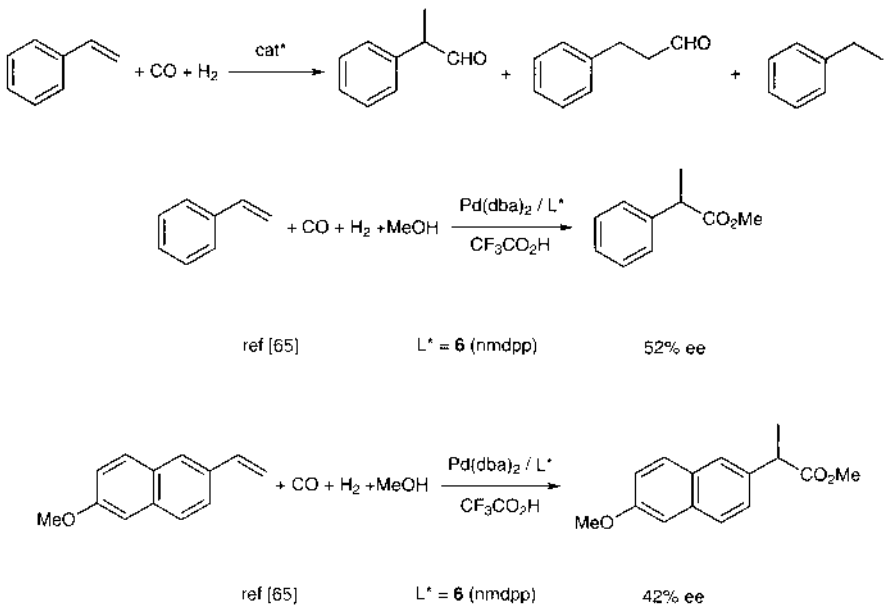

Fig. 10. Hydroformylation Reactions

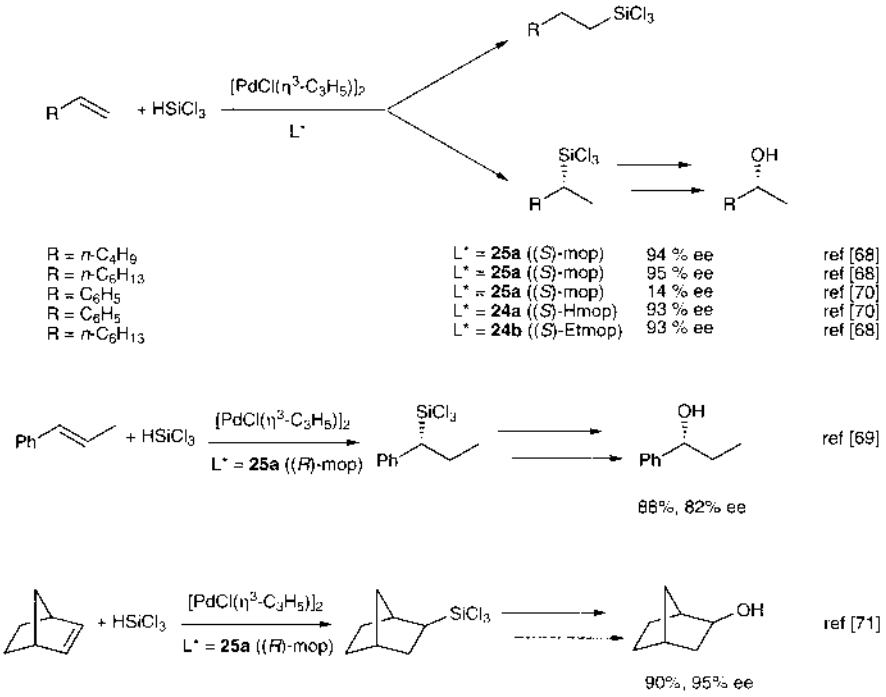

Fig. 11. Asymmetric Hydrosilylation Reactions of C=C Double Bonds

presence of a resident chelating diphosphine, while a monophosphine allows the formation of a square-planar intermediate $HPd(SiCl_3)(L^*)(RCH{=}CH_2)$. Reactions could be runned at 40 °C with 0.1% equiv. of catalyst. The products are easily transformed by a two-step procedure into the corresponding alkanol, with retention of configuration. Some representative results on alkenes are listed in Fig. 11. It is interesting to point out that mop **25a** and **24b** gave almost the same enantioselectivity (95% ee (*R*) and 93% ee (*R*) respectively) in the reaction on 1-octene. This a good evidence here that the methoxy group of mop is not acting as a coordinating group. This chemistry was successfully extended to 1-arylalkenes and to norbornene (Fig. 11).[69—71] It was found that a mop analog **24a** where the methoxy group is missing (H-mop) is superior to the usual mop ligand **25a** (MeO-mop) in the hydrosilylation of styrene (Fig. 11). Finally a phenanthrene analog **28** of mop has been found useful in hydrosilylation of cyclic-1,3-dienes.[72]

Hydrosilylation of C=O Double Bonds Catalytic asymmetric hydrosilylation of ketones was first reported in 1972 with the use of catalysts of the type $[L^*PtCl_2]_2$, where L* stands for a monophosphine (bmpp **1f** or mppp **1a**).[73] Dichloromethylsilane reacts on alkyl phenyl ketones to give after hydrolysis the corresponding alcohols with a modest enantioselectivity (ee<20%). It was soon discovered by Ojima *et al*. that rhodium catalysts such as $[(bmpp)_2RhCl$-

(solvent)] and the proper choice of a silane transformed some ketones or α-ketoesters into alcohols of enantioselectivities up to 60% ee.[74—76] A ferrocenylphosphine **30a** gave a low enantioselectivity (5% ee) in the reaction of trimethylsilane on propiophenone.[77] Usually the highest ee's were obtained with silanes bearing a phenyl group connected to silicon. Some selected examples are listed in Fig. 12. A survey of the catalytic asymmetric silylation of ketones including many data on the use of monophosphines as ligands as well as mechanistic discussions (assuming a *trans* relationship between the two monophosphines[78]) can be found in a review published in 1977.[79]

Since the late seventies there were no much research in that area since diop and other bidentate ligands gave superior results. Moreover chiral nitrogen ligands became of growing importance[80] However there is still a good potential for the exploration of catalytic properties of the many new monophosphines which were subsequently synthesized. They were no reports concerning hydrosilylation of imines.

4.7. Hydroacylation In this section is reported an unusual reaction which, formally, is the addition of a C–H bond of an aromatic ring on an alkene. The only case of such an enantioeselective process has been described by Brunner *et al*.[81] It involved the reaction between iodobenzene and norbornene in the presence of formic acid and an amine. When glyphos **16** was the ligand of the palladium catalyst, *exo*-5-norbornane (10% ee) was produced. A bidentate ligand such as norphos gave around 35% ee.

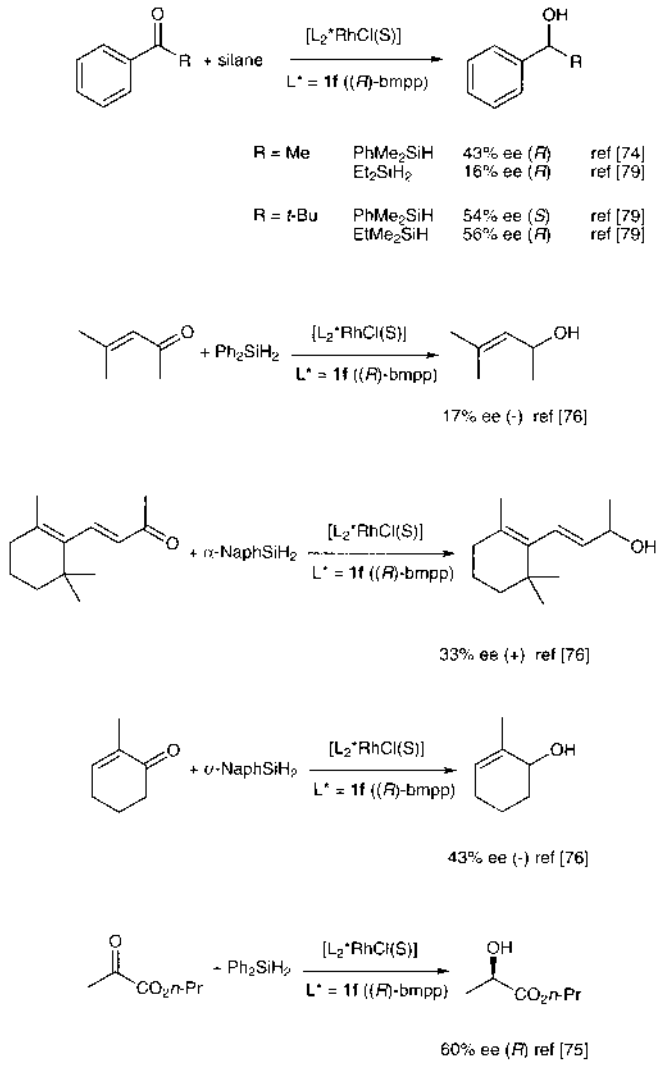

Fig. 12. Asymmetric Hydrosilylation Reactions of C=O Double Bonds

5. Conclusion

Monodentate chiral phosphines of various types are presently known and found some application in organometallic catalysis. The structural diversity is well evidenced by inspection of the structures reported in Figs. 1—4.

Monodentate chiral phosphines were for a long time neglected, because bidentate diphosphines were very successful in asymmetric hydrogenation and for some other reactions, as explained in the introduction of the present article. However one may consider that they are some good indications that suitable monodentate chiral phosphines should play a useful role in the future. They are already the ligands of choice for controlling asymmetric hydrosilylation of carbon carbon double bonds.[80b] They also gave excellent results in cross-coupling reactions and allylic substitutions. We can expect that they will play a role of increasing importance in many aspects of organometallic catalysis. We hope that this review will encourage practitioners of asymmetric catalysis to consider the potential interest of chiral monodentate phosphines and to investigate this area which has been quite neglected till now.[82]

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