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Review

Preparation of optically pure *P*-stereogenic trivalent phosphorus compounds

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Contents

Abstract

This review describes the main synthetic methodologies available for the preparation of *P*-stereogenic phosphines and derivatives. The literature coverage focuses in the last ten years. Apart from the discussion of the methods, a table with the compounds reported and their application in homogeneous catalysis is also given.

Keywords: *P*-stereogenic ligands; Organic synthesis; Transition-metal complexes; Homogeneous catalysis

1. Introduction

The simple idea that a phosphorus atom surrounded by three different substituents is configurationally stable and can lead to a pair of enantiomeric forms has been discussed for well over 100 years, and was verified experimentally by Meisenheimer and Lichtenstadt in 1911 [1]. Since then, the interest of substances possessing a stereogenic [2] phosphorus atom has evolved from studies about phosphorus stereochemistry to the preparation of optically pure *P*-stereogenic substances as ligands in transition-metal homogeneous catalysis. Precisely the early development, in the late 1960s and the 1970s, of asymmetric hydrogenation with *P*-stereogenic phosphines [3,4] like DIPAMP [5–7] promoted active research in this field, creating expectations about the utility of this kind of ligands in catalysis [8]. Soon after, however, interest in *P*-stereogenic ligands fell away because of the synthetic difficulties encountered and the publication of a first generation of backbone-chiral phosphines, such as DIOP [9], CHIRAPHOS [10], DUPHOS [11–13] and the ubiquitous BINAP [14]. As a result, *P*-stereogenic ligands have been greatly outnumbered by ligands with a stereogenic backbone and were less studied than these.

Nevertheless, several research groups have been working towards the preparation of enantiomerically pure *P*-stereogenic compounds and the last 15 years have seen a rebirth of interest in these substances. In 1994, Pietrusiewicz and Zablocka published

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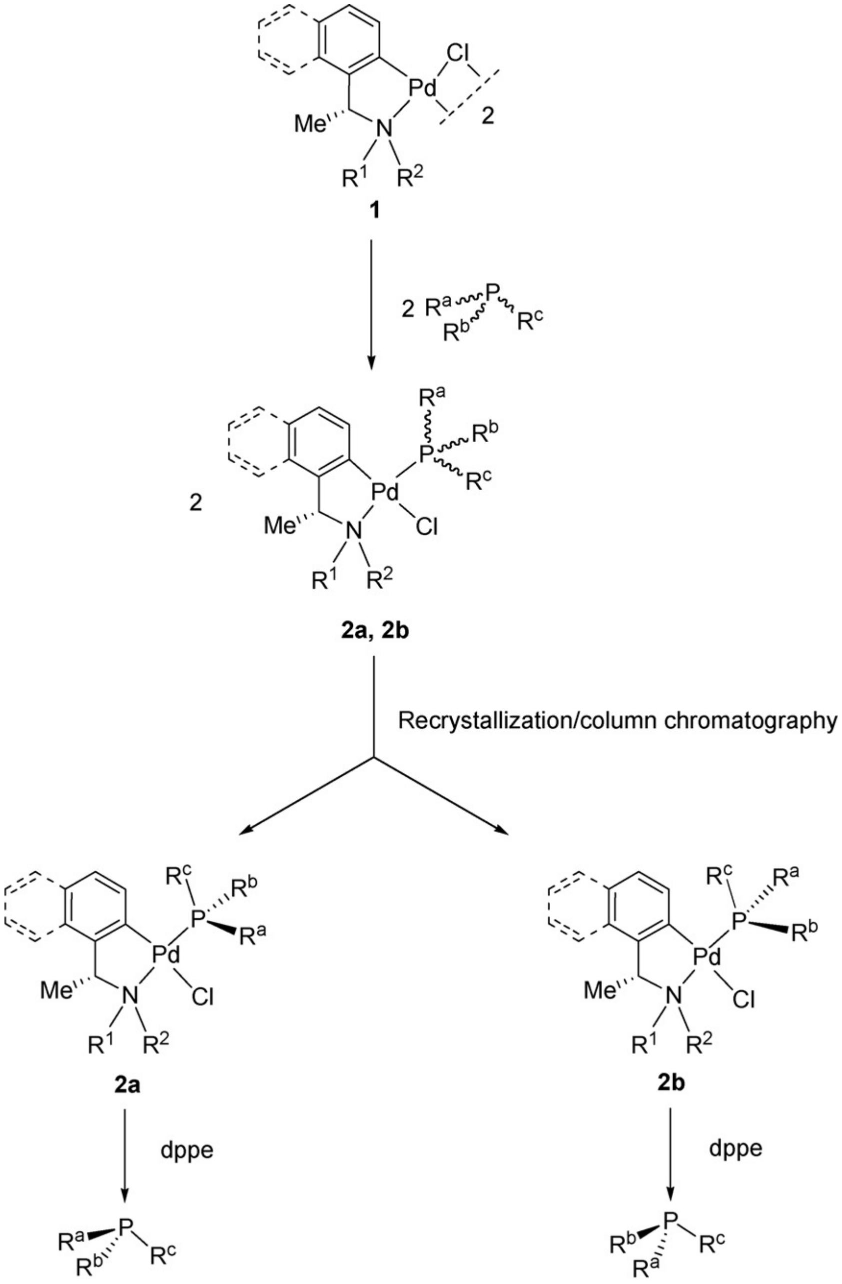
a very comprehensive review on *P*-stereogenic phosphines and derivatives [15]. Other, more recent reviews have dealt with aspects of synthesis and use in catalysis of *P*-stereogenic compounds [16]. Some of these deal with phosphine–boranes [17–20] – which have become key intermediates in the synthesis of *P*-stereogenic phosphines – while others are devoted to particular types of ligands [21] or their catalytic applications [22–24].

This review aims to give an overall view of the main methods of preparation available, some of them very well established. It focuses on the preparation of *P*-stereogenic ligands through asymmetric synthesis and catalysis. The literature covered runs from 1995 to beginning of 2006, although some relevant earlier observations are also included. Although the review is mainly devoted to P(III) phosphines and derivatives (with P–N, P–O and other bonds), some P(V) compounds – oxides and sulfides – are also discussed, as they are intermediates in phosphine synthesis. A list of phosphines and some derivatives is also provided to reflect the potential of each of the methods discussed. In this list, usually only the last product in a multistep synthesis is shown.

2. Preparation by resolution of racemates

The first methods reported for the preparation of optically pure phosphines bearing stereogenic phosphorus atoms involved the synthesis of the desired product in racemic form, followed by the resolution of this racemate by means of a chiral auxiliary. This synthetic route, generally speaking, suffers from serious



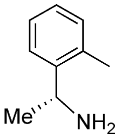
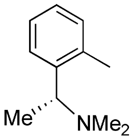
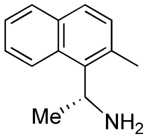
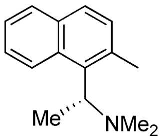
Scheme 1. Resolution of phosphines by means of chiral palladacycles.

drawbacks. It requires tedious recrystallizations or chromatographic separations and gives low overall yields. Moreover, its success is highly dependent on the groups attached to the phosphorus atom and on the choice of the chiral auxiliary, which gives very little opportunity for changing the structure of the groups bound to the phosphorus atom. Pietrusiewicz and Zablocka's excellent review [15] gave a wide variety of examples of resolution of racemic mixtures for obtaining optically pure *P*-stereogenic phosphines and derivatives.

The serious problems stated above, however, mean that this method is not used unless necessary, with the exception of the use of palladium metallacycles, which will be outlined below. Nevertheless, a very recent use of the resolution method with a tartaric acid derivative, to prepare a very strained, *P*-stereogenic phosphine has been reported by Imamoto et al. [25]. The resolution of racemates is attractive if preparative HPLC systems are available [26,27]. This method, though expensive, is used at an industrial level (it has already been used in laboratory scale) to obtain optically pure phosphine derivatives in large quantities.

Up to now, palladium(II) complexes containing enantiomerically pure forms of orthometallated 1-phenylethylamines and 1-naphthylethylamines [28,29] are considered the most efficient resolving agents, at least for certain types of phosphines [30]. The general procedure is depicted in Scheme 1. The desired phosphine, in racemic form, is made to react with the cyclometallated dimer **1**, which provides a pair of mononuclear complexes **2** in 1:1 proportion (sometimes, only half equivalent of the resolving agent is used and then, ideally, only one enantiomer of the phosphine reacts while the other remains in solution). Complexes **2** differ only in the absolute configuration of the P atom and are thus diastereomeric, allowing, in principle, separation by standard methods, such as column chromatography or recrystallization. Once separated, the phosphine is displaced from the palladium by means of dppe or another strongly coordinating agent, yielding the desired enantiomerically pure phosphine. This method has been widely used to resolve both monodentate and bidentate phosphines because the dimers **1** are straightforward to prepare and because the mononuclear complexes **2** are usually easy to characterize and crystallize, for ascertainment of the absolute configuration of the phosphorus atom. Even when X-rays are not available, a detailed 2D NMR study of **2** generally allows the deduction of the absolute configuration of the phosphorus atom.

Table 1
Resolution of *P*-stereogenic phosphines

Resolving agent, PdL	PBnMesPh		PBnCyPh	
L	*R*	*S*	*R*	*S*
	–	–	–	84% yield >90% d.e.
	–	–	70% yield >95% d.e.	–
	80% yield 60% d.e.	32% yield >95% d.e.	66% yield >95% d.e.	70% yield >95% d.e.
	86% yield >95% d.e.	40% yield >95% d.e.	–	–

The array of phosphines resolved by this method is quite large and they are usually obtained in high optical purity. Wild [30] has reviewed the resolution of phosphines and arsines with this method.

Some of these enantiomerically pure phosphines, obtained by us, were used in palladium asymmetric hydrovinylation [31,32]. A summary of the results obtained is given in Table 1.

3. Preparation by stereoselective synthesis

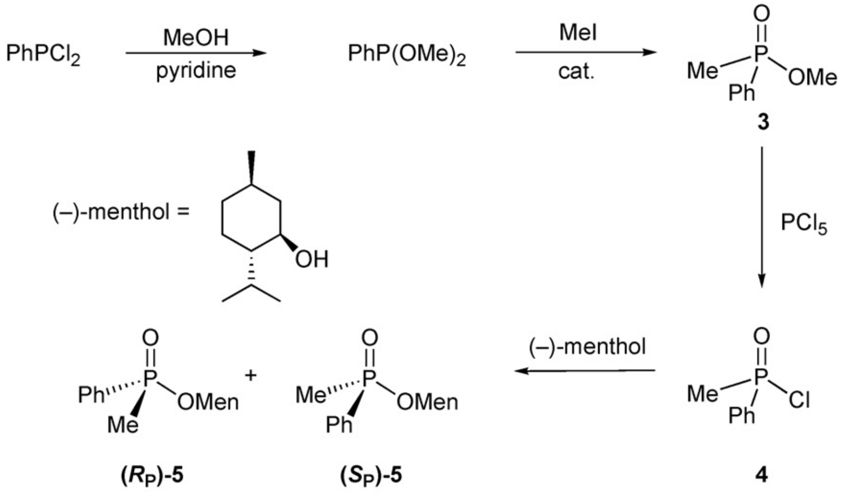
The lack of flexibility of the methods involving resolutions of racemic mixtures led to the development of synthetic routes using a stoichiometric amount of a chiral auxiliary, which allowed the preparation of a suitable *P*-resolved precursor. From this precursor, via stereoselective substitutions, new C–P bonds were created to lead to the desired phosphine. In the following sections, the use of menthol, ephedrine and sparteine as chiral auxiliaries to prepare such precursors is discussed. As a stoichiometric amount of chiral auxiliary is needed, it is desirable to recycle this auxiliary. To date, the systems most commonly employed are the pairs menthol/dihalophosphine [17,33,34], sparteine/dimethylphosphine–borane [35–37], sparteine/racemic secondary phosphine–borane [38] and ephedrine/diaminophosphine [39–42]. It is noteworthy that phosphine–boranes have emerged as suitable intermediates in the synthesis of *P*-stereogenic phosphines.

3.1. Use of menthol as a chiral auxiliary

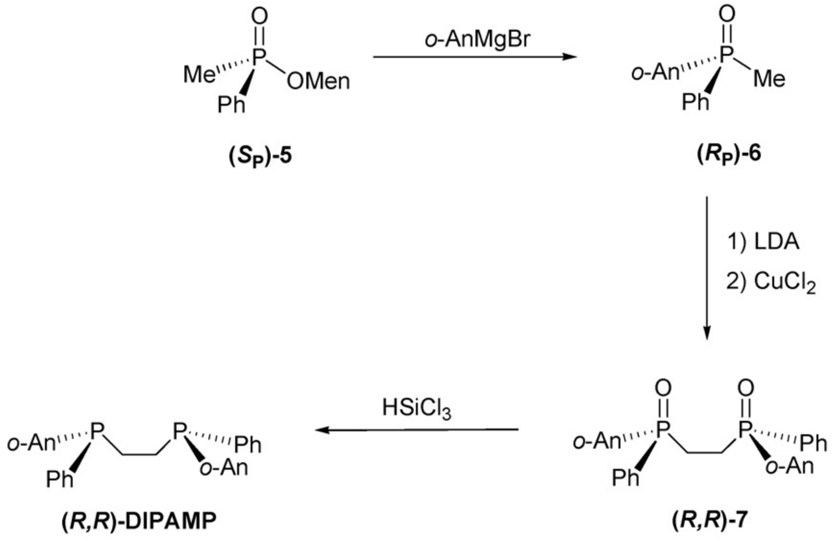
The idea outlined above was first explored by Nudelman and Cram [43] and Mislow and co-workers [44,45] in the late 1960s, using menthol as a chiral auxiliary. They were the first to demonstrate that unsymmetrically substituted menthylphosphinates (**5**, Scheme 2) could be separated into their diastereomeric forms by recrystallization. Starting from this study, Horner and Schlotthauer [46] and others [47,48] synthesised and separated other pairs of menthylphosphinates.

Usually, only one of the diastereomers (in Scheme 2, for example, (S_P)-**5**) was obtained in its the pure form, whereas the other remained in the mother liquors.

Once one of the menthylphosphinates had been obtained in a pure form, it was found that it could be reacted stereospecifically with Grignard reagents to furnish the tertiary phosphine oxides with complete inversion of the configuration at the phosphorus atom.



Scheme 2. Synthesis of menthylphosphinates.

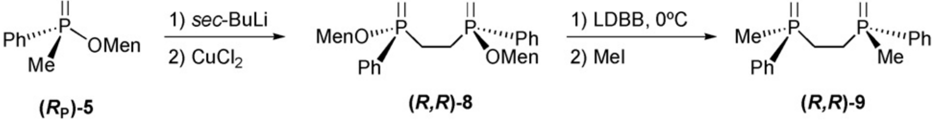


Scheme 3. First synthesis of DIPAMP.

In fact, Knowles and co-workers used this procedure [47] in one of the steps of the synthesis of DIPAMP, as shown in Scheme 3.

The reactions of this type had to be carried out with excess of Grignard reagent and under some harsh conditions. Furthermore, success was very sensitive to the groups attached to the phosphorus atom, oxygen and moisture. In spite of these drawbacks, the high level of stereospecificity usually attainable with this method and its flexibility attracted the attention of many groups. Consequently, a large number of menthylphosphinates and phosphine oxides were prepared.

Imamoto's group was able to replace the menthyl group at the phosphorus atom while retaining configuration [33,49] by reductive stereospecific cleavage. They found that one-electron reducing agents performed such a transformation. Upon examining several reducing agents (alkali metals and Li-NH_3 among others), it was found that lithium 4,4′-di-*tert*-butyldiphenylide (LDBB) was the reagent of choice because it preserved the stereochemical integrity of the phosphorus atom. Scheme 4 shows the use of this method to prepare diphosphine oxides. The diphosphide obtained upon treatment with LDBB was quenched with methyl iodide to furnish the diphosphine oxide (*R*,*R*)-**9**. Several



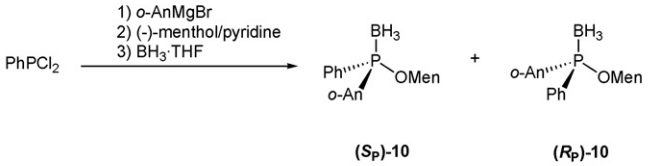
Scheme 4. Imamoto's strategy for synthesising diphosphine oxides.

other diphosphine oxides were obtained. This method is complementary to the nucleophilic substitution of the menthyl group, in which the substitution at the phosphorus atom occurs with inversion of configuration.

In a seminal paper, in 1990, Imamoto et al. [17] went a step further in menthol methodology by using phosphine–boranes instead of phosphine oxides. This was the first example of the use of phosphine–boranes as versatile intermediates in the synthesis of *P*-stereogenic phosphines. Phosphine–boranes were found to be much more suitable intermediates than oxides. They are crystalline and chemically and configurationally stable even under severe conditions (oxidant, acid or basic media). These features enable work with phosphine–boranes without inert atmosphere, using classic methods like crystallizations and column chromatography to purify the intermediates. Moreover, the use of phosphine–boranes avoids the handling of the malodorous, air-sensitive and sometimes corrosive free phosphines until they are needed. The removal of the boranato group (see Section 4) is easily achieved by stirring phosphine–borane in a large excess of an amine [17], such as diethylamine, morpholine or DABCO or, in more basic phosphine–boranes, using certain acids [50]. This step fully retained the configuration at the phosphorus atoms, in contrast to the stereochemical problems associated with reduction of oxides.

The strategy of Imamoto et al. began with the synthesis of the phosphinite-boranes [17] as it is shown in Equation 1 .

The diastereomeric phosphinite-boranes **10** were separated by means of chromatography and R_P-**10** was then converted to (*S*,*S*)-DIPAMP as depicted in Scheme 5.



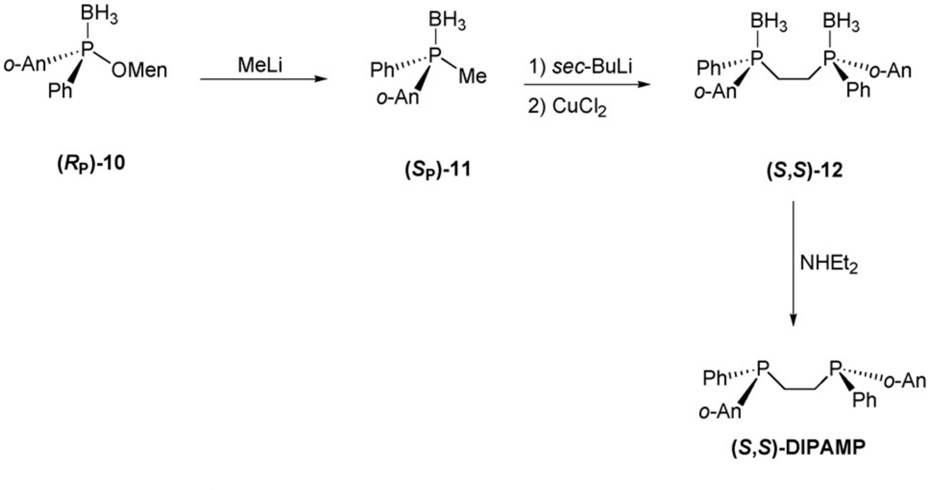
Equation 1. Synthesis of menthylphosphinite-boranes.

The same group also succeeded in removing the menthyl group reductively [49], at low temperature, with total preservation of phosphorus configurational integrity (Scheme 6), in an analogous way to what they did with menthylphosphinates (Scheme 4). The anionic tricoordinated phosphorus species **14** were subsequently allowed to react with methanol or alkyl halides, still at low temperature, to afford optically active secondary (**15**) or tertiary (**16**) phosphine–boranes, both in high optical purity, with an e.e. value above 90% in most cases.

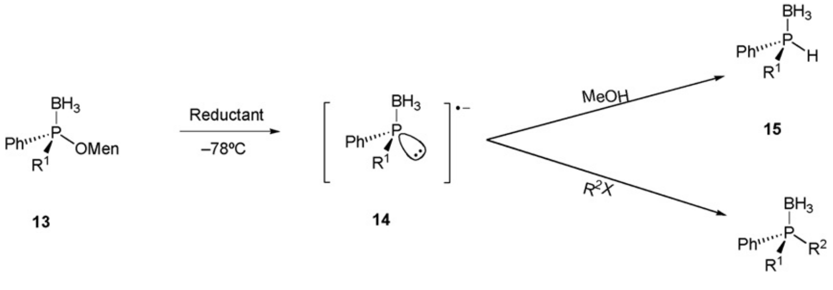
The reductants explored were LDBB, Li-NH_3 and lithium naphthalenide. The reaction was complete in 5 min. Upon raising the temperature, it was found that the anionic species **14** quickly racemized, presumably via pyramidal inversion.

3.2. Use of heterobifunctional chiral auxiliaries

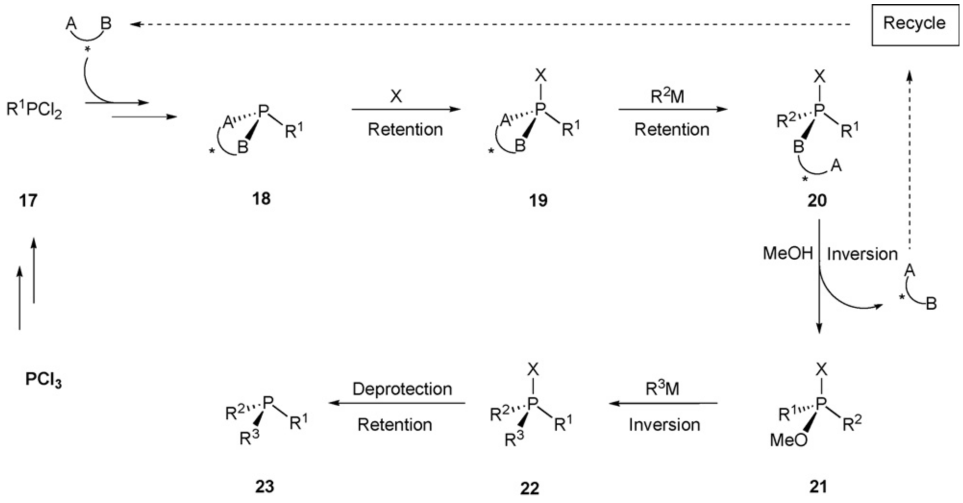
The previous section showed that nucleophilic substitution of an alkoxy group, either in a phosphinate or in a phosphinite-borane, usually proceeds with high stereoselectivity, with inversion of configuration at the phosphorus atom. This led to expectations that two sequential substitutions could also provide a means



Scheme 5. Synthesis of (*S*,*S*)-DIPAMP using phosphine–borane methodology.



Scheme 6. Reductive cleavage of menthyl group in menthylphosphinite-boranes.



Scheme 7. Preparation of *P*-stereogenic phosphines using a chiral bifunctional auxiliary.

for stereoselective synthesis of phosphine derivatives. For such an approach to work, an appropriately resolved *P*-stereogenic precursor, possessing two potentially different leaving groups was a prerequisite. This idea crystallized in the work of several laboratories [39,51,52], which used heterobifunctional chiral auxiliaries, with the formation of cyclic derivatives (phospholidines). The phospholidines were formed in very high diastereomerical purity, allowing the resolution of the phosphorus atom. The general strategy is depicted in Scheme 7.

Starting from PCl_3 – which can be *formally* regarded as the starting point for the preparation of P(III) compounds, by three stepwise nucleophilic substitutions – dichlorophosphines **17** can be obtained via Grignard or organolithium reagents (when compound **17** is not commercially available). The diastereomerically pure (with the phosphorus atom resolved) cyclic phospholidine **18** is then prepared by using the suitable chiral auxiliary A–B. Then, this compound is conveniently protected with the protecting group X. Compound **19** is, indeed, the starting *resolved P-stereogenic precursor*, *possessing two different leaving groups* as defined in the preceding paragraph. The use of the protective group, X, was found to be necessary to stabilize the configuration of the phosphorus atom during the synthesis and has the additional advantage of protecting the phosphine from oxidation. Starting from **19**, two nucleophilic attacks and a methanolysis step produce the protected phosphine **22**, which is stereospecifically deprotected to furnish the desired phosphine **23**. The reaction steps were highly regio- and stereoselective and an e.e. greater than 90% for **23** was generally observed.

Three groups successfully followed this scheme. The exact conditions they used are summarized in Table 2.

Protected, diastereomerically pure cyclic derivatives **19** were prepared from (−)-ephedrine **24** (Brown [51] and Jugé [39] groups), or from the camphor derivative **25** (Corey [52] group). These chiral auxiliaries are shown in Fig. 1. The choice between boranato, sulfide and oxide is *formally* a choice between P(III) (boranato) and P(V) (oxide or sulfide).

Examination of the literature on each of the three methodologies depicted in Table 2 shows that the most successful method, in terms of its versatility, stereoselectivity and simplicity and availability of the chiral auxiliary is the approach of Jugé et al. [39] which is why it is the most widely used [40–42,53–63].

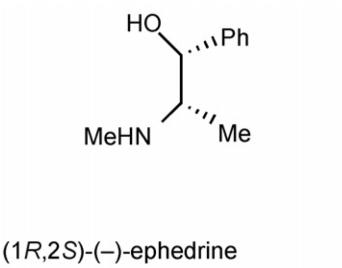
Table 2
Stereoselective synthesis of *P*-stereogenic phosphines via cyclic chiral auxiliaries

Author	A	B	X	M	Deprotection
Jugé et al. [39]	O	N	BH_3	Li	$NHEt_2$
Corey et al. [52]	S	O	S, BH_3	Li	Si_2Cl_6
Brown and co-workers [51]	O	N	O	MgBr	–[a]

[a] Deprotection was not carried out.

This powerful method for the preparation of *P*-stereogenic phosphines [39] is shown in Scheme 8. In the original method, R^1 was Ph, but some variations have been made [53,62] and, in principle, it is applicable to other substituents. In the following discussion, however, it will be assumed that R^1 is phenyl.

The key intermediate is oxazaphospholidine-borane **26**, prepared by a one-pot reaction from bis(diethylamino)-phenylphosphine, and (−)-ephedrine, at 105 °C, followed by protection with BH_3. The ring closing takes place stereoselectively [39,40], with preferential formation of the R_P diastereomer, in 90% d.e. The absolute configuration at the phosphorus atom has been determined by chemical correlation and NMR analysis [64] and corroborated by single crystal X-ray diffraction of **26** [65,66]. The high stereoselectivity in the formation of



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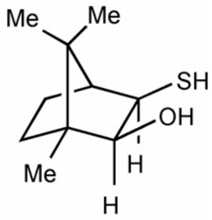

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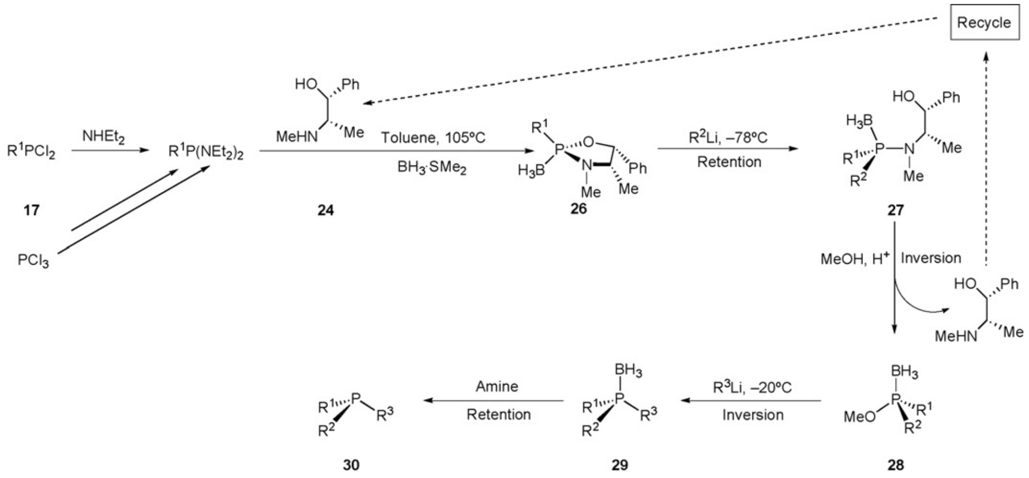
Fig. 1. Chiral auxiliaries used to prepare the *P*-resolved precursors **19**.

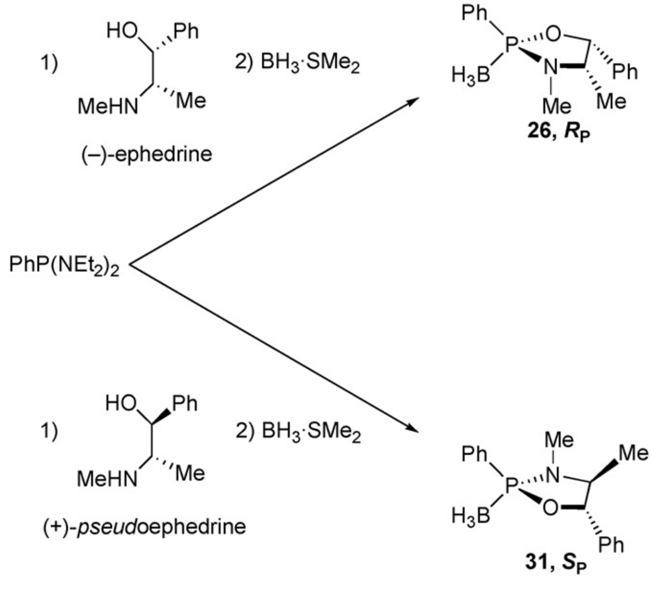


Scheme 8. The method developed by Jugé for the synthesis of *P*-stereogenic phosphines.

26 can be explained by steric reasons because the phenyl group is in the opposite position from the substituents of (−)-ephedrine [56]. To gain further insight into this question, Hansen and co-workers prepared [56] compound **31**, which is analogous to **26** but uses (+)-(1*S*,2*S*)-*pseudo*ephedrine (Scheme 9).

Hansen et al. found that the absolute configuration of the phosphorus atom was the opposite to what it was in **26**. Hence, they concluded that the configuration at Ph-substituted C(1) in ephedrine controlled the absolute configuration at the phosphorus atom, in such a way that the preferred isomer is the one in which the Ph in C(1) and the Ph in the phosphorus atom are in *trans*.

As already depicted in Scheme 8, alkyl and aryl lithium reagents cleanly opened the oxazaphospholidine-borane ring **26**, at −78 °C in THF, to give the corresponding phosphamide-boranes **27**. Jugé's group discovered that this step is totally regioselective [40], as it breaks the P–O bond, whereas the P–N bond remains intact. The stereoselectivity of the reaction was also studied by X-ray analysis [40,56] of some phosphamide-boranes **27**. The reaction occurs with retention of configuration at the phosphorus atom and with a d.e. greater than 85%. This stands in sharp contrast with other acyclic chiral phosphorus derivatives, whose P–C forming reactions with organometallic compounds occur with inversion of configuration at the phosphorus atom. Grignard reagents also react with **26**, but only at higher temperatures [40]. In this case, important losses of stereoselectivity are observed, so organolithium reagents are the nucleophilic reagents of choice.



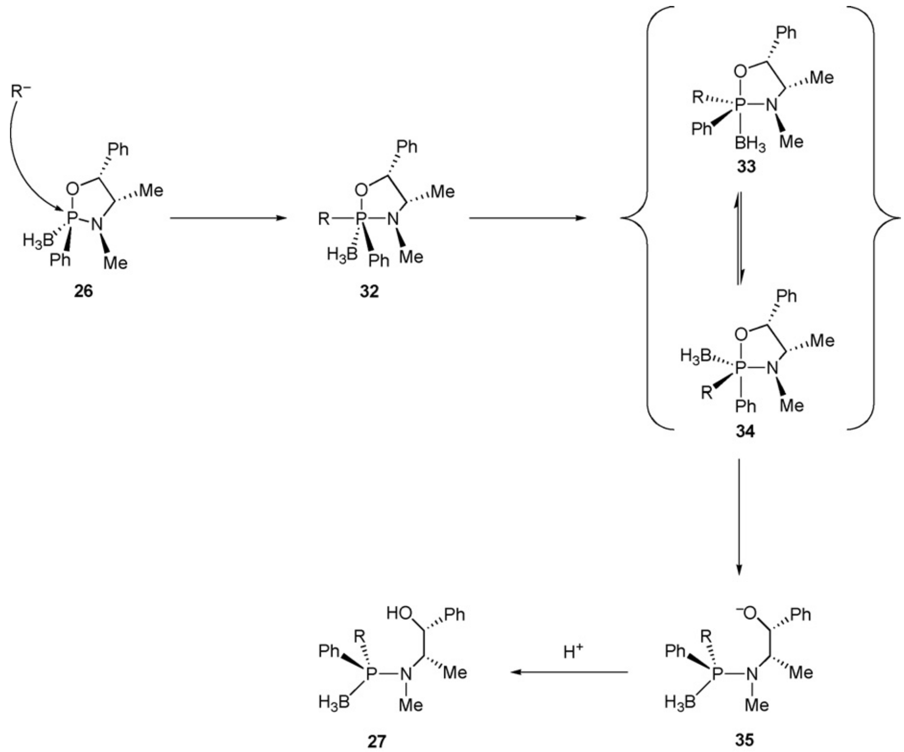
Scheme 9. The different oxazaphospholidine-boranes prepared by Hansen.

To account for the observed retention of configuration, the mechanism depicted in Scheme 10 was proposed [40].

The crystal structure of the starting complex **26** shows a distorted oxazaphospholidine ring, where the methyl substituent of the nitrogen is anti to the O leaving group. Consequently, it was deduced that the stereochemistry of the P–C bond formation is under kinetic control and the nucleophilic attack of R$^-$ occurs on the less hindered side of the P–O bond, which is opposite to the nitrogen atom, with the formation of the pentacoordinate intermediate **32**. This compound stereopermutes into one another (**33** or **34**), which has the substituents on the phosphorus atom in a staggered position with respect to the *N*-methyl group. The presence of the oxygen group in the apical position of the intermediate permits the cleavage of the P–O bond and the formation of compound **35** with retention of configuration. Brown and co-workers reached a similar conclusion on studying the reaction between an oxazaphospholidine oxide and Grignard reagents [51]. This mechanism agrees with the known of stereochemistry of substitution reactions at the phosphorus atom with other cyclic compounds [67,68].

As mentioned above, a variety of alkyl- and aryllithium reagents with diverse electronic and steric properties react smoothly with **26**, but some limitations have been found. The first of these arose in the preparation of *P*-stereogenic analogues of dppf (Equation 2).

It was discovered that 1,1′-dilithioferrocene did react with **26**, though a poor yield and stereoselectivity were found for the reaction [55,58]. Jugé and co-workers [58] only reported the overall yield of the bisaminophosphine–boranes **36**, whereas van



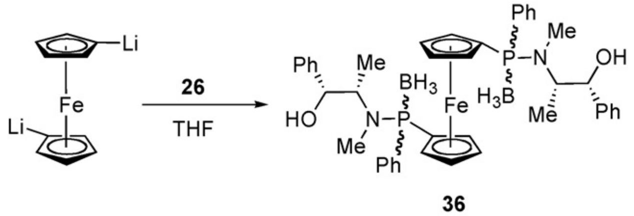
Scheme 10. Proposed mechanism for the nucleophilic alkylation of oxazaphospholidine-borane **26**.

Leeuwen and co-workers [55] estimated the diastereomeric ratio R_P,R_P:*pseudomeso* of **36** at 65:35. These rather disappointing results were explained by the steric hindrance of the ferrocene, which requires higher temperatures for the reaction to proceed, implying a major decrease in stereoselectivity. However, using other approaches, ferrocene has been successfully introduced (in terms of yield and stereoselectivity) by several groups, as will be commented on later.

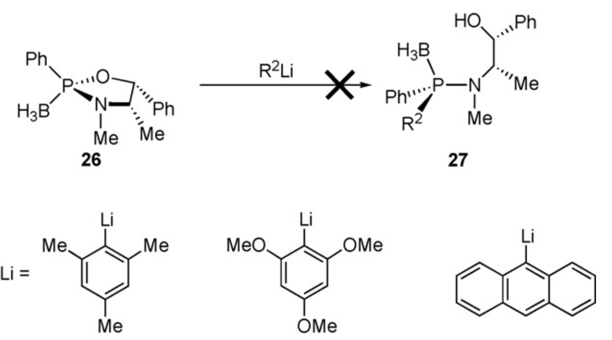
Another limitation of this first nucleophilic step was pointed out more recently by Mezzetti's group [53], on preparing phosphines bearing highly symmetric, bulky substituents. It was found that *o*,*o*′-disubstituted aryllithium compounds did not react with **26**, as shown in Equation 3.

This result contrasts strikingly with the easy introduction of an *o*-substituted aryl group (*o*-anisyl, 1-naphthyl, etc.), reported by other groups [55,57,60,63], and restricts the applicability of the oxazaphospholidine approach.

Following the general method depicted in Scheme 8, the next step in the synthesis is the acidic methanolysis of **27** to produce phosphinite-boranes **28**, as shown in Equation 4.

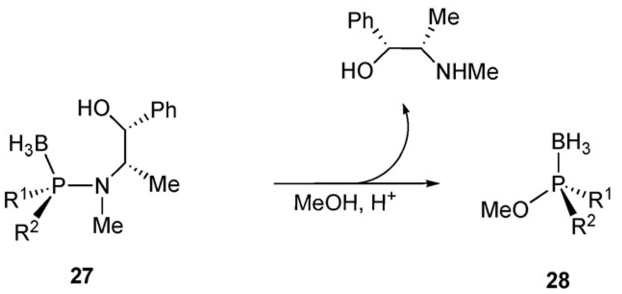


Equation 2. Introduction of a ferrocene moiety to **26**.

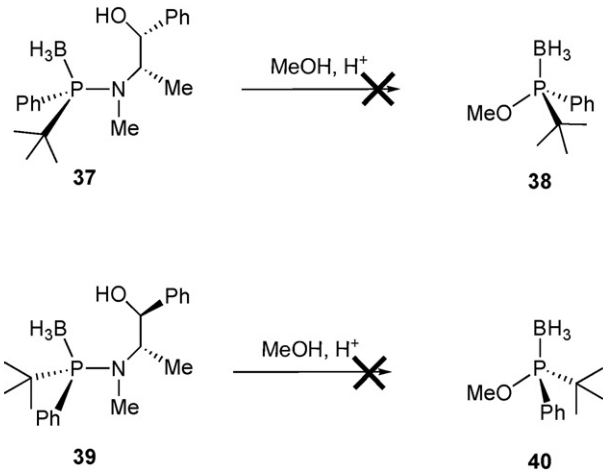


Equation 3. Unsuccessful attempts to introduce *o*′,*o*′-disubstituted aryls at the phosphorus atom.

Reaction conditions are straightforward: aminophosphine–boranes **27** are dissolved in methanol and one equivalent of sulfuric acid is added at 0 °C or at room temperature. One equivalent of (−)-ephedrine is released and can be recycled.



Equation 4. Acidic methanolysis of **27** to yield the phosphinite-boranes **28**.



Equation 5. Unsuccessful attempts to synthesise phosphinite-boranes bearing a *tert*-butyl group.

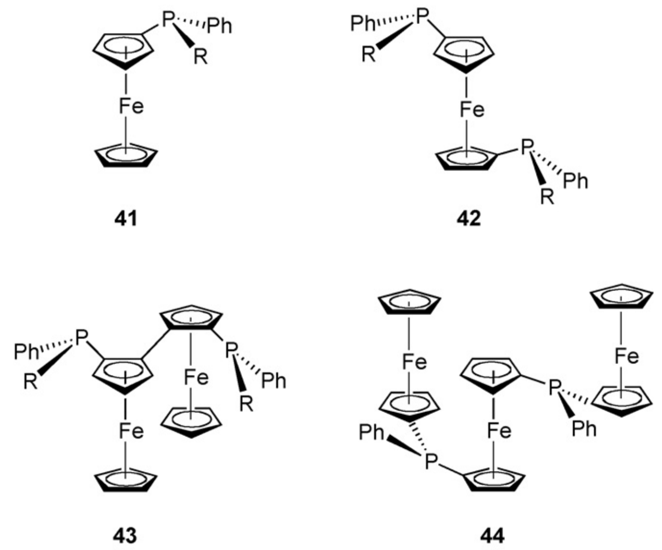


Fig. 2. *P*-stereogenic phosphines containing ferrocene.

Generally, this step works without any problem, affording **28** in high yield and stereoselectivity with inversion of configuration at the phosphorus atom, because it is considered a S_N2 process. An exception to the straightforwardness of the reaction was found by Rippert et al. [56], who observed that the introduction of a *tert*-butyl group precludes the methanolysis step (Equation 5).

Neither **37** (derived from (−)-ephedrine) nor **39** (derived from (+)-*pseudo*ephedrine) react with methanol, even at reflux. The steric hindrance and the basicity of the *tert*-butyl group probably account for this lack of reactivity.

Phosphinite-boranes **28** react with organolithium reagents at low temperature, to afford tertiary phosphine–boranes **29**, with clean inversion of configuration at the phosphorus atom, as shown in Equation 6.

The reaction has proved to be quite general, both aryl and alkyl lithium derivatives give the desired reaction. An exception, found by Mezzetti's group [53], is that in parallel to what is shown in Equation 3, *o*,*o*′-disubstituted aryllithium reagents do not react with phosphinites, either. They persisted in trying to obtain *P*-stereogenic phosphines with *o*,*o*′-disubstituted groups by synthesising the oxazaphospholidine **26** with R^1 = mesityl and continuing with the scheme depicted in Scheme 8. Although they met with some success, the strategy was abandoned because of low yields on opening compound **26** and at the subsequent methanolysis step [53].

It seems clear that Jugé's method does not allow the introduction of *o*,*o*′-disubstituted aryl groups, which restricts its use for synthesising highly crowded phosphines. Another limitation has been recently pointed out by us [63] while preparing crowded phosphines by Jugé's method. An unexpected phosphine–borane resulting from the attack of isoproyllithium on an aromatic group was obtained.

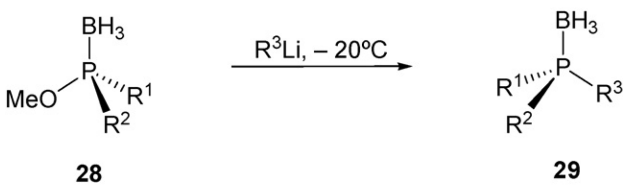
Introducing a ferrocene, which, as stated earlier, was a troublesome issue, met with more success when ferrocenyllithium (or 1,1′-dilithiumferrocene) was introduced in this second nucleophilic substitution (Equation 6). Although some loss of optical purity was observed, chromatographic techniques allowed the preparation of the desired enantiomerically pure phosphine–boranes. In this way, mono and bidentate ferrocenyl phosphines, some of them shown in Fig. 2, were successfully prepared and used in some transition metal-catalyzed reactions [55,60–62,69–71].

In phosphines **41**, R is an aryl or alkyl group, whereas in phosphines **43**, R is an aryl group.

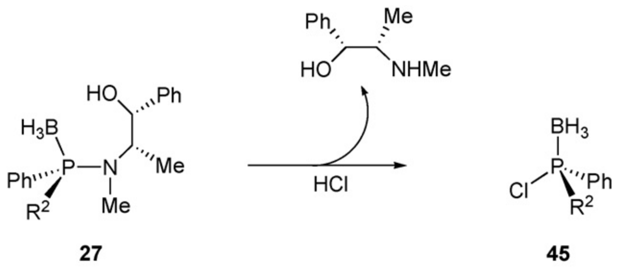
In an extension of the basic method, Moulin, Jugé and co-workers recently developed [41,42,72,73] (Equation 7) a strategy for the preparation of enantiomerically pure chlorophosphine–boranes **45**.

The preparation of chlorophosphine–boranes is *formally* similar to the methanolysis step, but with the difference that chlorophosphine–boranes **45** are much more reactive towards nucleophiles than the corresponding phosphinite-boranes **28**.

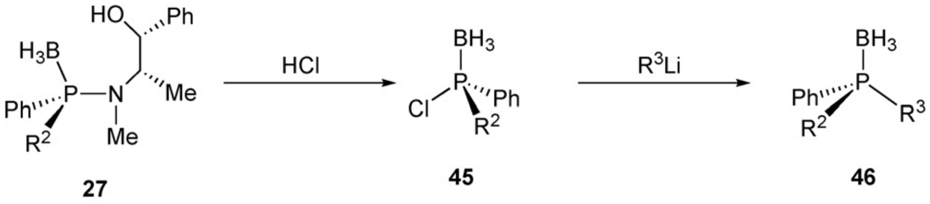
As the chlorophosphine–boranes are highly reactive, usual hydrochloric acid solutions in water cannot be used and so dry sources of HCl are needed. Toluene solutions of HCl, obtained



Equation 6. Reaction of phosphinite-boranes **28** with organolithium reagents.



Equation 7. Stereoselective synthesis of chlorophosphine–boranes.



Scheme 11. Preparation of *P*-stereogenic phosphine–boranes from chlorophosphine–boranes.

by bubbling pure HCl through toluene, were originally used after titration, but recently Mezzetti and co-workers [53] successfully used commercial solutions of HCl in diethyl ether as a more practical reagent.

Despite the formal similarity between the methanolysis step to produce phosphinite-boranes **28** and the acidolysis step to produce chlorophosphine–boranes **45**, several differences need to be considered.

First, the stability of compounds **28** and **45** is very different. Whereas phosphinite-boranes **28** are completely stable compounds which can be recrystallized, chromatographed and stored with no special care, chlorophosphine–boranes **45** are much more sensitive to atmospheric conditions and have to be handled with care. Attempts to purify this kind of compound, by column chromatography, have met with decomposition and/or racemization.

Second, the stereoselectivity in their formation deserves special attention. Generally speaking, the excellent stereoselectivity attained in the preparation of phosphinite-boranes **28** is not achieved in the chlorophosphine–boranes, although with cautious control of the exact experimental conditions good results are also obtained.

These reasons account for the very few applications of chiral chlorophosphine–boranes in the literature. Nevertheless, they are useful synthons when they are used in situ, without isolation. Jugé and co-workers showed [72] – by calculation – that the asymmetrically substituted chlorophosphines (R^1R^2PCl) without the protection of the borane group are extremely prone to racemization when traces of HCl (almost impossible to avoid under experimental conditions) are present, precluding their synthetic utility.

The stereoselectivity of the formation of chlorophosphine–boranes **45** depends on the groups attached to the phosphorus atom, the molar excess of HCl, the concentration of reagents and the reaction time. Jugé and co-workers investigated these factors systematically [73] and drew some general conclusions. Due to the sensitivity of this kind of compound, chlorophosphine–boranes were quenched with alkyllithium compounds to perform the analysis of yield and selectivity (Scheme 11). It was assumed that this step was quantitative and with full inversion of configuration at the phosphorus atom. Table 3 shows the best conditions (in terms of stereoselectivity) for each substituent R^2 at the phosphorus atom.

As shown in Scheme 11, chlorophosphine–boranes react instantaneously with organolithium reagents to furnish phosphine–boranes with inversion of configuration at the phosphorus atom. This makes compounds **45** attractive synthons when the phosphinite-boranes **28** are not reactive enough. Furthermore, chlorophosphines **45** also react with other milder nucleophiles such as alkoxides or thiolates, opening up the possibility of easy synthesis of a large number of *P*-stereogenic compounds [73].

The Vogt [59] and Jugé [41] groups used the synthon **35** (Scheme 10) in the synthesis of new aminophosphine-phosphinite ligands (AMPP). These kinds of compounds contain either one (**50**) or two (**48**) stereogenic phosphorus atoms, as shown in Scheme 12.

These AMPP ligands were coordinated to rhodium and successfully used in catalytic hydrogenation [41] and hydroformylation [59,74].

3.3. Stereoselective deprotonation of enantiotopic methyl groups

The starting point of this section is the observation, published in 1968 by Mislow and co-workers [45], that deprotonation of the P–Me group in phosphine oxides occurs with total preservation of configurational integrity of the neighbouring stereogenic phosphorus centre (Scheme 13). The α-carbanion derived from **51** reacts with electrophiles to give α-functionalized phosphines.

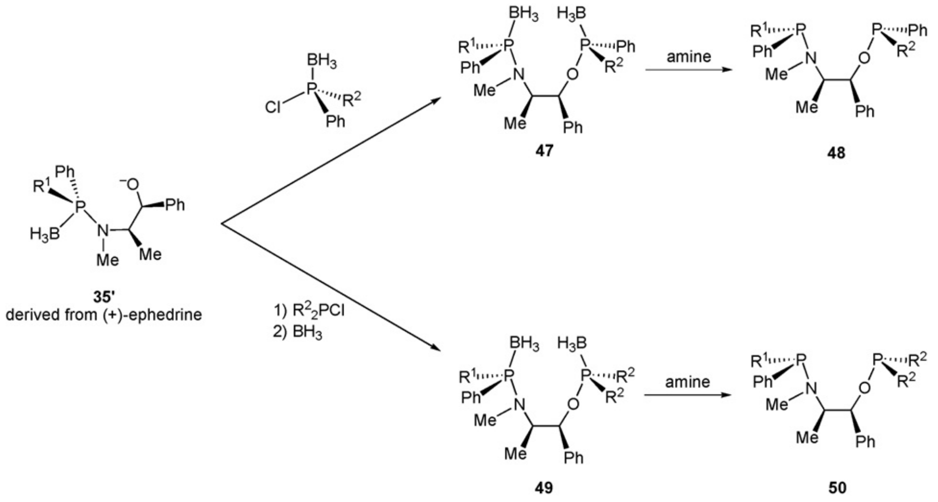
One important application of this relative *acidity* of methyl protons came in 1973, when Mislow and co-workers discovered that methylphosphine oxides can be oxidatively coupled with copper salts via their α-carbanions to yield directly the corresponding resolved symmetric, *P*-stereogenic 1,2-diphosphinoethane oxides **55** (Scheme 14) [75].

This step was used by Vineyard et al. (Schemes 3 and 4; see Section 3.1) in their preparation of DIPAMP [47] and was later adapted by other groups to synthesise several C_2 symmetric diphosphines.

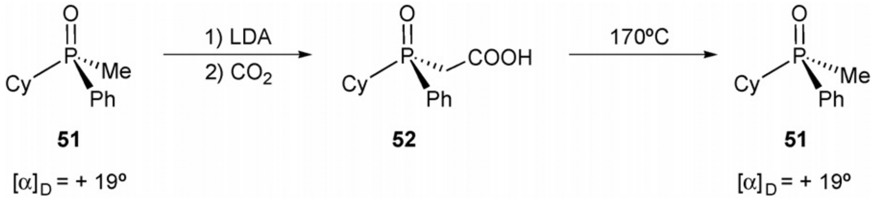
It was found that in analogy to the oxides, methylphosphine–boranes are readily deprotonated by strong bases [17,76]. This relative acidity is attributed to the electron-withdrawing effect

Table 3
Conditions for the synthesis of chlorophosphine–boranes **45**

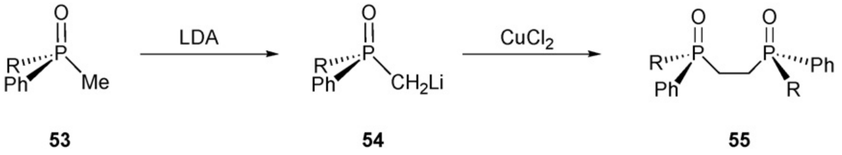
R^2	Equivalent HCl	[HCl] (mM)	R^3	Yield of **46** (%)	e.e. (%)
Methyl	2.1	20	*o*-Anisyl	80	90
o-Anisyl	2.1	180	Me	90	98
o-Tolyl	6.0	60	Me	61	98
1-Naphthyl	2.1	20	Me	50	0
2-Naphthyl	3	130	Me	46	85
2-Biphenylyl	6	20	Me	41	99
Cyclohexyl	6	60	Me	46	80
tert-Butyl	6	60	–	–	–



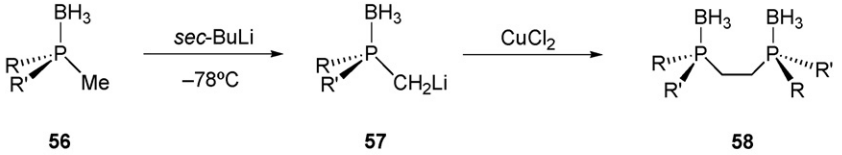
Scheme 12. The synthesis of AMPP ligands.



Scheme 13. First example of deprotonation of a P–Me group of a *P*-stereogenic compound.



Scheme 14. Copper promoted oxidative coupling of phosphinomethylide oxides.



Scheme 15. Copper-promoted oxidative coupling of phosphinomethylide-boranes.

of the P–B bond, which activates adjacent C–H bonds [19]. In phosphine–boranes, deprotonations are usually carried out using organolithium reagents, particularly *sec*-butyllithium and *n*-butyllithium. The highly nucleophilic carbanions **57** obtained react with electrophiles to give α-functionalized products and can also be oxidatively coupled by copper (Scheme 15).

The deprotonation of methylphosphine–boranes allows the synthesis of a wide variety of optically pure *P*-stereogenic compounds, provided that *an enantiomerically pure P-stereogenic methylphosphine–borane is available*. To avoid this limitation, in 1995 Evans and co-workers [77] introduced (−)-sparteine (Fig. 3) as chiral auxiliary.

The approach of the Evans group [77] is shown in Scheme 16. It is based on enantioselective deprotonation of aryldimethylphosphine–boranes, using *sec*-BuLi and (−)-sparteine as a chiral auxiliary. Sparteine effectively complexes the lithium atom [78,79] while deprotonation takes place and, in this chiral environment, *sec*-BuLi differentiates between the two

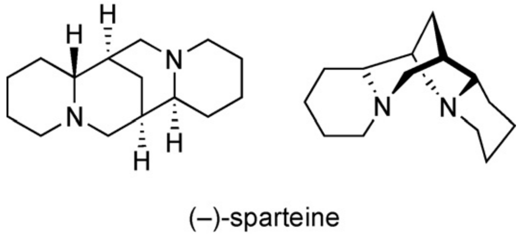
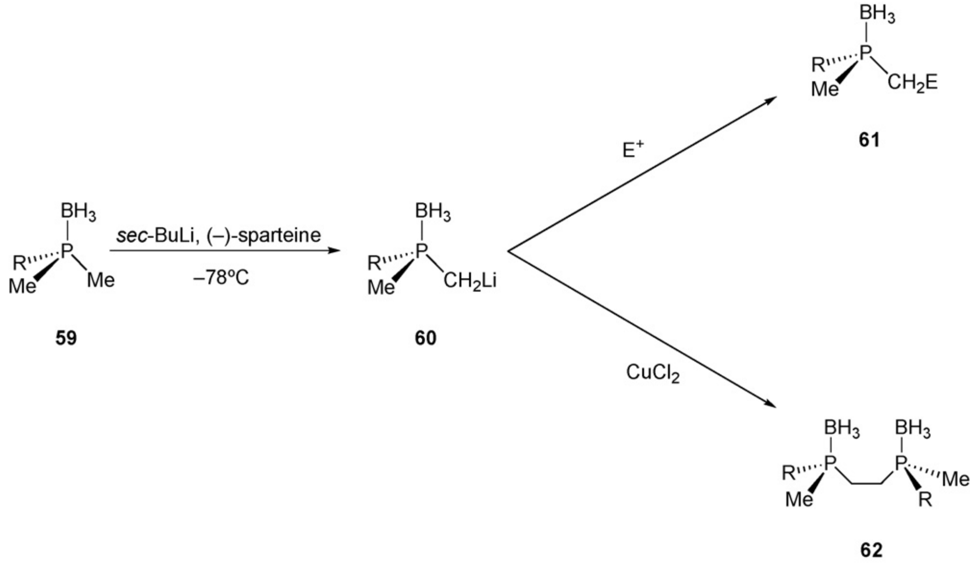


Fig. 3. Two views of the structure of (−)-sparteine.

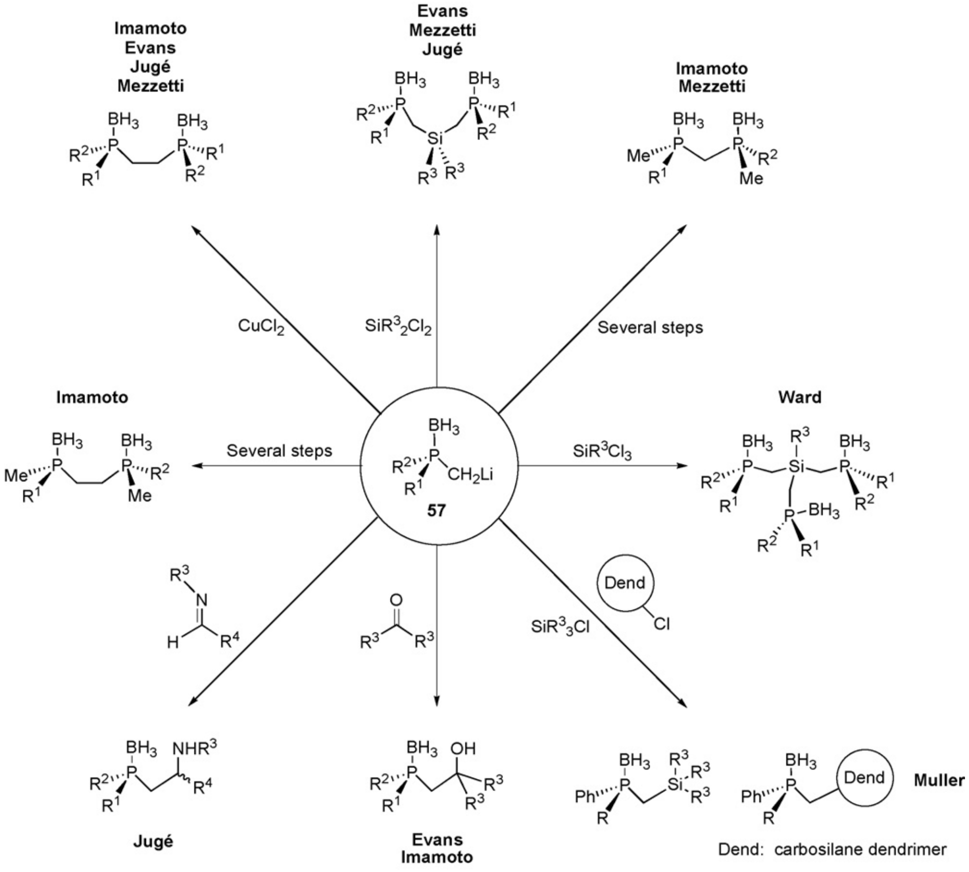


Scheme 16. Stereoselective deprotonation of an enantiotopic methyl group.

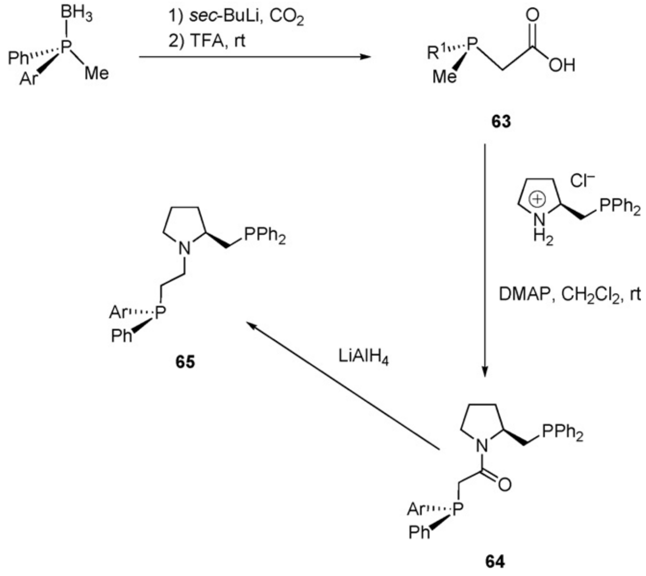
enantiotopic methyl groups. Hence, it deprotonates selectively one of them to generate a single *P*-stereogenic α-carbanion **60**, which reacts with an electrophile to yield **61** or produces the corresponding diphosphine–borane with a 1,2-ethanediyl bridge **62** by coupling with a Cu(II) salt.

By this method, a small family of diphosphine–boranes was prepared with good diastereomeric and enantiomeric excesses.

The scope of enantioselective deprotonation of dimethylphosphine–boranes has been greatly expanded by ongoing work at Imamoto's laboratories, as will be described later. However,



Scheme 17. Different *P*-stereogenic compounds obtained from deprotonation of methylphosphine–boranes by the groups of Evans [77], Imamoto [17,35,80,81], Jugé [39,82,83], Mezzetti [53,54,84,85], Ward [26] and Muller [63,86].



Scheme 18. Diphosphines obtained by Hii's group.

other groups have also taken advantage of the anions derived from methylphosphine–boranes, whether obtained with enantioselective deprotonation or by simple deprotonation of an already resolved *P*-stereogenic methylphosphine–borane. From these anions, a variety of derivatives have been prepared, as shown in Scheme 17.

We recently reported [86] the first dendrimers functionalized with *P*-stereogenic phosphines and their application in asymmetric Pd-catalyzed hydrovinylation.

In addition, a very recent paper by Hii and co-workers [87] described the preparation of *P*-stereogenic diarylphosphinoacetic-borane acids, **63**, and their proline derivatives (**64** and **65**) for palladium-catalyzed allylic alkylation, starting from a resolved methylphosphine–borane prepared using the Jugé method (Scheme 18).

In Evans' original study, one of the groups attached to each of the phosphorus atoms was an aryl group. In 1998 Imamoto et al. published [35,88] the approach depicted in Scheme 19, which allows the synthesis of C_2-type diphosphines bearing only alkyl groups at the phosphorus atoms (BisP*). Electronically they are electron-rich phosphines, which were complexed to rhodium and used in the catalytic asymmetric hydrogenation of several substrates, with a high degree of activity and enantioselectivity. Furthermore, they were used in detailed studies of the mechanism of enantioselection.

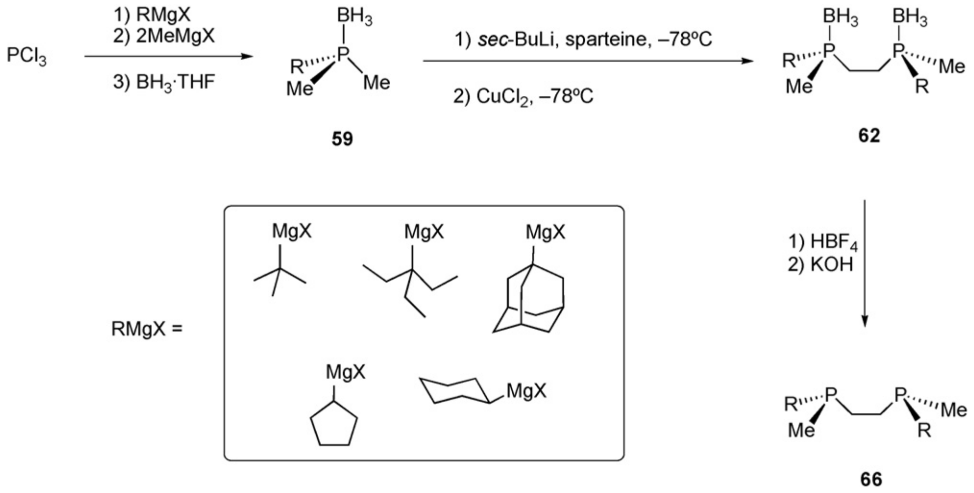
This strategy starts from simple materials to yield diphosphine–boranes **62** in a one-pot reaction with good yields and excellent enantioselectivities. Since the usual deboronation reaction with amines did not work properly with these electron-rich phosphines, the acidic method developed by McKinstry and Livinghouse [50] had to be applied (see Section 4).

The pure chiral diphosphine–boranes **62** were separated from the *meso* isomers by means of recrystallization. The absolute configurations at the phosphorus atoms were determined by single crystal X-ray analyses.

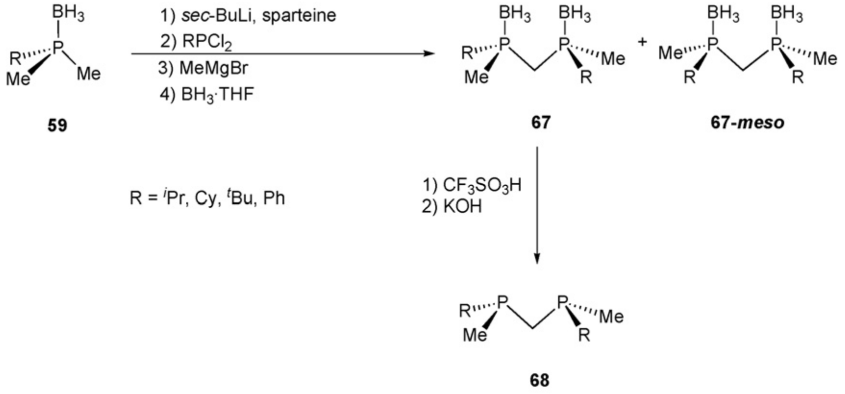
Starting from this work, Imamoto and Yamamoi succeeded in synthesising analogues of **66** but with the shortest alkyl bridge [80] (Scheme 20).

A ca. 1:1 mixture of the desired phosphine–boranes **67** and the *meso* isomer was obtained. This mixture was easily separated by recrystallization from methanol or ethanol and the desired phosphine–boranes **67** were obtained in optically pure form and deprotected to furnish pure diphosphines **68** (MiniPhos). X-ray structure determination was used to ascertain the absolute configuration at the phosphorus atom. The MiniPhos ligands were obtained as enantiomerically pure products, though with modest overall yields (<30%). These ligands were used in some representative catalytic asymmetric reactions (hydrogenation, hydrosilylation and Michael addition) and were found to exhibit, in some cases, excellent levels of enantioselectivity, despite being a lot simpler and smaller than previously reported chiral diphosphines.

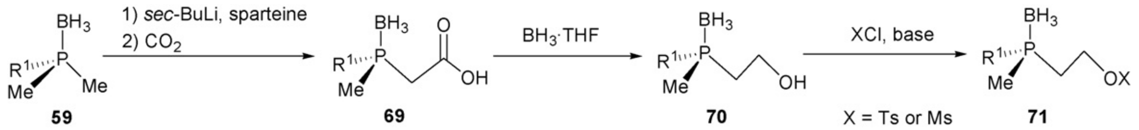
Imamoto and co-workers, after the good results obtained with the BisP* ligands, envisaged the synthesis of analogue phosphines but without the C_2 symmetry axis, i.e. with different substituents on each phosphorus atom [81,89]. To tackle this task, two precursors were prepared.



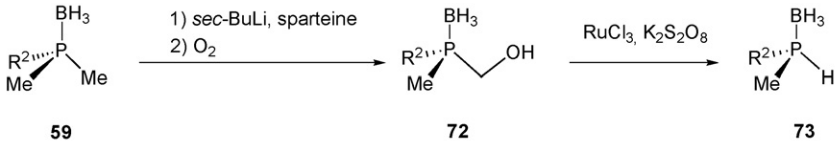
Scheme 19. Imamoto's approach to the synthesis of C_2, *P*-stereogenic diphosphines.



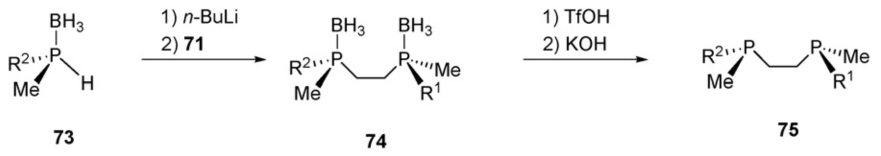
Scheme 20. Synthesis of methylene-bridged, *P*-stereogenic diphosphines.



Scheme 21. Synthesis of precursors **71** bearing a mesyl or tosyl group.



Scheme 22. Preparation of enantiomerically pure, secondary phosphine–boranes.



Scheme 23. Preparation of unsymmetric BisP* ligands.

The first were the phosphine–boranes **71**, bearing a good leaving group (mesylate or tosylate) on the β position [81,89]. Their synthesis is shown in Scheme 21.

The dimethylphosphine–boranes **59** were enantioselectively deprotonated with *sec*-BuLi in the presence of (−)-sparteine, and then bubbled with CO_2 to produce the phosphinoacetic-borane acids **69**. Reduction of these carboxylic acids by borane–THF complex afforded, in quantitative yield, the phosphinoethanol-boranes **70**, which were tosylated or mesylated to afford the desired compounds **71**.

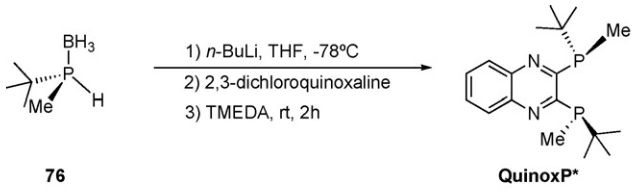
The second type of precursor needed was enantiomerically pure secondary phosphine–boranes **73** [90]. These were prepared using the method in Scheme 22.

The first step was the preparation of primary alcohols **72**, by oxidation with molecular oxygen of the organolithium compounds derived from **59**. These alcohols were oxidatively degraded to yield the secondary phosphine–boranes **73**.

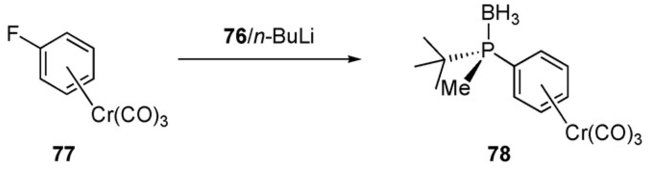
With products **71** and **73** in hand, Imamoto and co-workers prepared [81,89] (Scheme 23) the desired unsymmetric BisP*·BH_3. Deprotection furnished the free diphosphines **75**.

This kind of ligand was used in asymmetric, rhodium-catalyzed hydrogenation of several substrates. The results obtained were very promising, with high activities and enantioselectivities which were better, in some cases, than those obtained with C_2 counterparts.

The enantiomerically pure secondary phosphines **73**, once deprotonated, were also used to prepare a variety of diphosphines [91], taking advantage of their excellent nucleophilicity. One very recent example (Equation 8) is the synthesis of QuinoxP*, an excellent ligand for rhodium-catalyzed hydrogenation and other reactions [92].



Equation 8. Preparation of the QuinoxP* diphosphine.



Equation 9. Nucleophilic aromatic substitution in fluorobenzenechromium complexes.

Another example is the nucleophilic aromatic substitution in fluorobenzenechromium complexes [93], shown in Equation 9, starting from the same secondary phosphine–borane **76**.

Very recently a secondary diphosphine–borane has been used in the preparation of a *P*-stereogenic tetraphosphine and its use in Rh-catalyzed hydrogenation [94].

3.4. Dynamic resolution of P-stereogenic phosphides

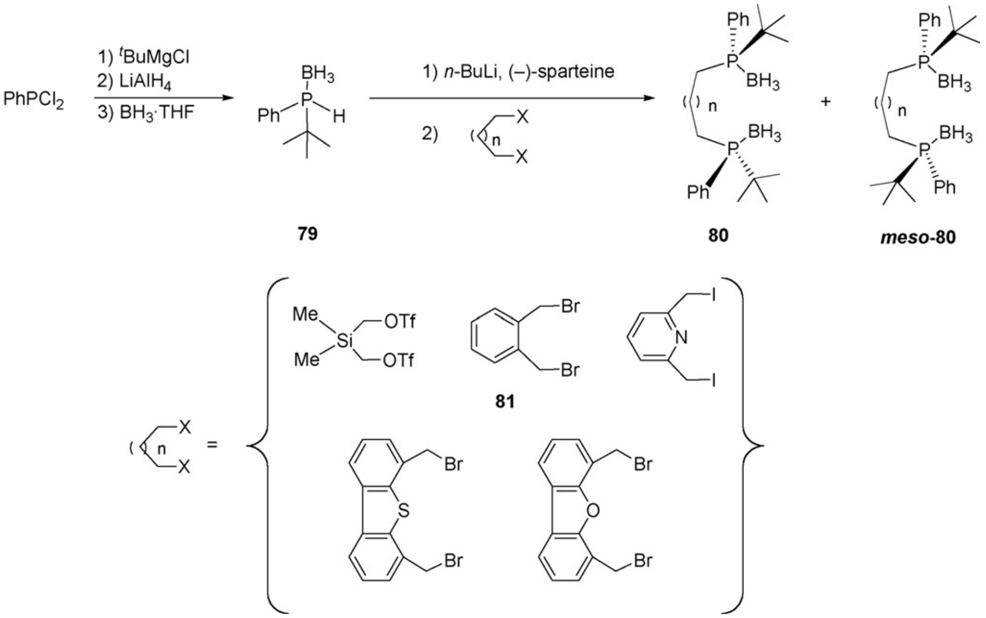
Enantioselective deprotonation with sparteine has also been used with *racemic* secondary phosphine–boranes. This method, discovered in the Livinghouse laboratories [38] and shown in Scheme 24, was successfully used to prepare several diphosphine–boranes bearing a *tert*-butyl and a phenyl group at the phosphorus atoms and different backbones between them. More recently, Lebel et al. [95] reported a crystallographic study of the compound obtained from a dibromo derivative similar to **81** but with the bromines in *meta*.

The racemic substrate selected was *tert*-butylphenylphosphine–borane, **79**, which was readily prepared from $PhPCl_2$ and *tert*-butylmagnesium chloride, with a final reduction with $LiAlH_4$. This compound was deprotonated by *n*-BuLi in presence of (−)-sparteine, at −78 °C. It was found that lithiated **79** could be dynamically resolved in good enantioselectivity. This enantioselectivity was temperature and time dependent. After systematic variation of these two parameters, it was deduced that the optimum conditions for equilibration to proceed were 1 h at room temperature. Afterwards, the suspension was cooled again at −78 °C and left to react with the dihalide or bis(triflate), to furnish **80** with very little impurity of *meso*-**80**.

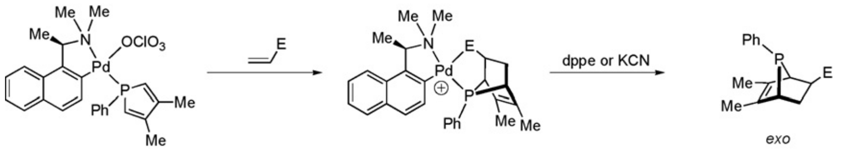
3.5. Orthometallated palladium complexes as chiral templates

Palladium(II) complexes containing enantiomerically pure forms of orthometallated amines, discussed in Section 2, were systematically employed by Leung [21] to prepare, in stereospecific fashion, certain types of phosphines and derivatives via the Diels–Alder reaction. Although 3,4-dimethyl-1-phospholane (DMPP) itself is not reactive enough in cycloaddition reactions, once coordinated to the Pd atom (**82**) it is readily activated [96], as seen in Scheme 25.

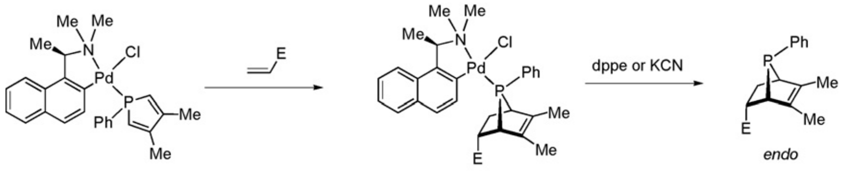
Since the perchlorate anion is labile enough to be displaced by a coordinating atom of the dienophile, the addition occurs stereospecifically to yield the pair of *exo* isomers intramolec-



Scheme 24. Preparation of diphosphine–boranes by means of deprotonation of secondary phosphines.



Scheme 25. Stereospecific preparation of an *exo* isomer of a phosphine.



Scheme 26. Stereospecific preparation of an *endo* isomer of a phosphine.

ularly with prior coordination of the dienophile [97–108]. The pair of cationic diastereomeric complexes **83** can be separated by the usual techniques, yielding only one enantiomer of the final phosphine **84**.

Interestingly, by changing the perchlorate anion for chloride, the reaction proceeds in *endo* diastereoselectivity [109–113] (Scheme 26), because the thermodynamically stable and kinetically inert Pd–Cl bond in **85** is not cleaved by the dienophile and the reaction takes place intermolecularly following the usual *endo* selectivity.

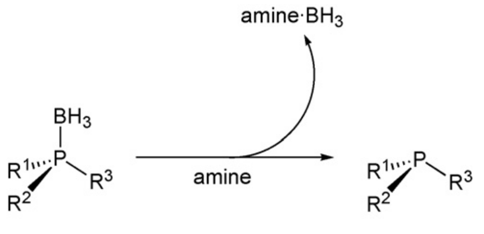
Leung's group greatly expanded the preparative scope of these two types of reactions and developed methods to prepare *P*-stereogenic diphosphines [114–122], phosphinoarsines, iminophosphines and enaminophosphines among other type of compounds [123]. A very recent report describes the use of an ionic liquid as a solvent and room temperature to promote an *endo* cycloaddition between DMPP and acrolein [124]. A recent new use for these chiral functionalized phosphines was in medicine, as some gold complexes of these ligands are active as anti-cancer drugs [125].

4. Deprotection of phosphine oxides and phosphine–boranes

If an enantiomerically pure phosphine oxide is prepared, it has to be reduced to the desired phosphine in a stereoselective way. Such transformation is usually carried out using silanes [126,127] (Scheme 3), sometimes mixed with amines [126,128]. In the literature, some methods proceed with retention of configuration at the phosphorus atom [126,128] and others provide inverted phosphines [126,128,129]. Nonetheless, these methods are not completely selective and some loss of optical purity is almost always observed [130]. Sometimes even racemization takes place [131], depending on the specific reducing agent used, the reaction time and the groups attached to the phosphorus atom. These drawbacks have been overcome with the use of phosphine–boranes [17–20,132] instead of phosphine oxides, as much more versatile intermediates.

The deboronation of the phosphine–boranes **29** to furnish the desired free phosphines **30** (Equation 10) is usually done by use of secondary amines, such as diethylamine or morpholine. The first examples were reported by Imamoto et al. [17], and since then, this procedure has become routine.

Although, in general, $R_3P{\cdot}BH_3$ adducts are more stable than the corresponding $R_3N{\cdot}BH_3$, the equilibrium shown in Equation 11 enables the BH_3 group to migrate to amines [19]. Hence, the free phosphine can be released by treatment of the phosphine–borane with a large excess of strong amines [18,19].



Equation 10. Deboronation of phosphine–boranes using amines.

$$R_3N{\cdot}BH_3 \quad + \quad R'_3P \quad \rightleftharpoons \quad R_3N \quad + \quad R'_3{\cdot}BH_3$$

Equation 11. Equilibrium between phosphine–boranes and free amines.

When secondary amines are not sufficiently effective, it has been found that cyclic, highly reactive amines such as DABCO or pyrrolidine are useful [18,133].

The reaction proceeds via the dissociation mechanism. In contrast to the reduction of phosphine oxides, the removal of the BH_3 group does not jeopardize the configurational integrity of the stereogenic phosphorus atom. The removal of the borane group has even been performed in a one-pot reaction, followed by complexation to a catalytically active metal to avoid the handling of the free phosphine [133,134]. Following this idea, in a recent paper, Jugé and co-workers [82] took advantage of the reducing properties of the borane group and prepared, in a one-pot reaction, phosphine complexes of Pd(0) and Rh(I) from Pd(II) and Rh(III) salts and *P*-stereogenic phosphine–boranes, in a general reaction described in Equation 12. The complexes were directly tested in catalytic reactions.

In electron-rich phosphine–boranes, the P–B bond is rather stable and, therefore, these compounds react sluggishly with amines. McKinstry and Livinghouse developed a procedure suitable for deprotecting this kind of compound [50]. They found that phosphine–boranes could be cleanly deprotected using certain acids such as methanesulfonic or tetrafluoroboric followed by neutralization with $NaHCO_3$ or K_2CO_3. The most efficient reagent, in terms of rate and yield, was $HBF_4{\cdot}OMe_2$. This method, complementary to the classic one with amines, is routinely used in Imamoto's laboratories in the preparation of a large family of *P*-stereogenic diphosphines, as discussed earlier. Decomplexation preserved completely the stereochemical

$$mR_3P{\cdot}BH_3 \quad + \quad MX_n \longrightarrow (R_3P)_mMX_{(n\text{-}m)} \quad + \quad mBH_2X \quad + \quad m/2H_2$$

Equation 12. Direct coordination of phosphines with concomitant reduction of the metal.

integrity of the stereogenic phosphorus atom, with total retention of configuration.

5. Preparation by asymmetric catalysis

A scrutiny of the main methods available for preparing enantiomerically pure *P*-stereogenic phosphines reveals that either resolution of racemates or asymmetric synthesis needs a stoichiometric amount of a chiral auxiliary, such as menthol, ephedrine or sparteine. These are expensive products when they are needed in multigram or kilogram quantities. Hence, an approach that would need a *catalytic* amount of a chiral product would be highly desirable. In principle, chiral catalysts could perform this function. In recent years, some reports in the literature suggest that this is a feasible approach.

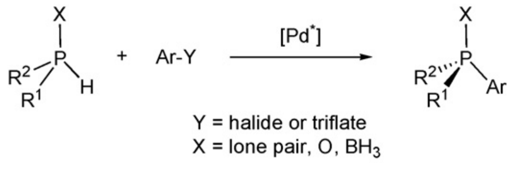
Glueck's group has published several papers [135–139] on this idea. Initial work on hydrophosphination [135] catalyzed by a chiral platinum complex achieved modest success (in terms of activity and enantioselectivity), but demonstrated that the reaction was catalytic.

More recently, palladium-catalyzed asymmetric phosphination has met with very promising results. This reaction is a cross-coupling of a secondary, racemic phosphine (or derivative) with an aryl halide or triflate, to prepare a tertiary, *P*-stereogenic phosphine with control of the stereochemistry at the phosphorus atom, as shown in Equation 13. In principle, the use of chiral palladium catalysts could lead to enantioenriched products starting from racemic secondary phosphines or derivatives as discussed below.

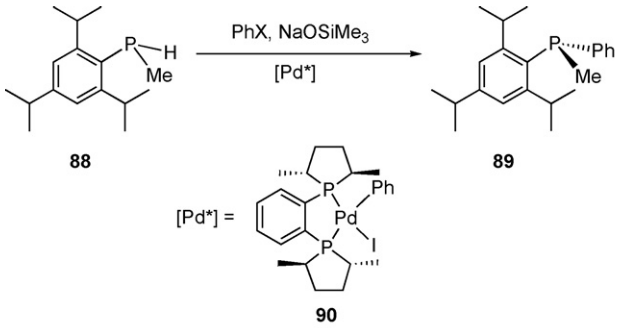
P-stereogenic, secondary phosphine oxides undergo palladium-catalyzed coupling with aryl or vinyl halides or triflates with retention of configuration at the phosphorus atom [140]. With phosphine–boranes, however, Imamoto et al. observed [141] that coupling enantiopure P(BH_3)HMePh with *o*-iodoanisole led to PAMP–BH_3 with retention or inversion of configuration at the phosphorus atom, depending on the base, solvent and temperature. More recently, Livinghouse and co-workers showed [142] that adding Cu(I) to similar reaction mixtures gave tertiary phosphine–boranes in high stereoselectivity also with retention.

One of the reactions studied in Glueck's laboratories [136] to prepare enantioenriched products from racemic secondary phosphines is shown in Equation 14. Racemic **88**, containing the bulky group 2,4,6-tris(isopropyl)phenyl, is coupled with a phenyl group to furnish enantioenriched phosphine **89**, in a reaction catalyzed by the palladium complex **90**.

It should not be forgotten that the introduction of 2,6 substituted groups is cumbersome (see Section 3.2). Furthermore, product **89** is a precursor of bidentate phosphines, by coupling with Cu(II).



Equation 13. Pd-catalyzed asymmetric phosphination.



Equation 14. Pd-catalyzed asymmetric phosphination.

The catalyst was the (*R*,*R*)-Me-DUPHOS palladium complex **90**. The reaction was easily monitored with ^{31}P NMR spectroscopy. The conditions used and the results obtained are listed in Table 4.

With 5 mol% of **90**, a typical reaction was complete in about 1 h. Toluene was the preferred solvent (entries 1–3), with increase and reduction of the e.e. at lower and at higher temperatures (entries 4 and 5, respectively). Phenyl bromide and triflate could also be used, although with them e.e.'s were lower (entries 5 and 6).

Some mechanistic studies were performed, which suggested a possible catalytic cycle, shown in Scheme 27. At low temperature, ^{31}P NMR study of the individual steps in this mechanism provided some insight into the origin of stereoselectivity.

Treatment of catalyst **90** with phosphine **88** displaced the iodide to form the cationic complex **C** as a nearly 1:1 mixture of diastereomers. This complex is deprotonated by $NaOSiMe_3$ to give the phosphido complex **D**. Neither the intermediate **90** nor the phosphine **88** react with $NaOSiMe_3$ and thus the formation of **D** appears to proceed by this two-step process.

The phosphido complex **D** exists as a 40:1 mixture of diastereomers, which presumably interconvert through inversion at the phosphorus atom, as was known for a similar type of complex. Reductive elimination of tertiary phosphine **89** occurred at temperatures above −20 °C. Oxidative addition of PhI occurs smoothly to regenerate catalyst **90**. Complex **A** was also detected, meaning that **D** can also react with two equiva-

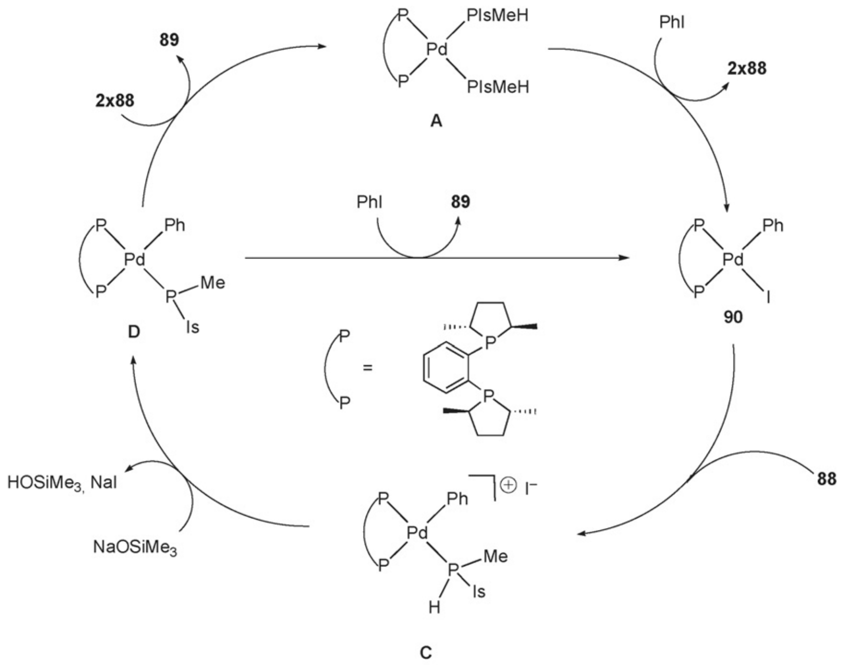
Table 4
Pd-catalyzed asymmetric synthesis of **89** from **88**

Entry[a]	X	Solvent	*T* (°C)	Yield (%)	e.e. (%)
1	I	THF	21	69[b]	66
2	I	MeCN	21	60[b]	58
3	I	Toluene	21	71[b]	73
4	I	Toluene	4	84[c]	78
5	Br	Toluene	50	60[c]	42
6	OTf	Toluene	50	53[c]	38

[a] Base = $NaOSiMe_3$ (1 M in THF); catalyst = **90** (5% for all entries except entries 1 and 2); 2 equivalents of PhX except in entry 4.

[b] By ^{1}H NMR integration after column chromatography.

[c] Isolated yield after column chromatography.



Scheme 27. Catalytic cycle proposed for Pd-catalyzed asymmetric phosphination. Is = 2,4,6-tris(isopropyl)phenyl.

lents of phosphine **88** to generate **A**, which is known to react readily with PhI to form catalyst **90**.

Regarding the origin of enantioselectivity, two extreme routes are conceivable. If the two diastereomers of **D** undergo reductive elimination at similar rates, faster than the inversion at the phosphorus atom, the e.e. of product **89** would reflect their thermodynamic ratio. Alternatively, if interconversion of the two diastereomers of **D** by inversion at the phosphorus atom is faster than reductive elimination, their relative rates of reductive elimination could control the e.e.

To work out the better route, the relative rates of inversion at the phosphorus atom and reductive elimination in complex **D** were evaluated. Deprotonating a 1:1.4 diastereomeric mixture of complex **C** produced a 1:6 enantiomeric mixture of the final phosphine **89**. This implies that inversion at the phosphorus atom in complex **D** is equal or faster than reductive elimination because otherwise the initial ratio of diastereomers of **C** would have been carried through the product. Thus, the mechanism of enantioselection can be described as a dynamic resolution.

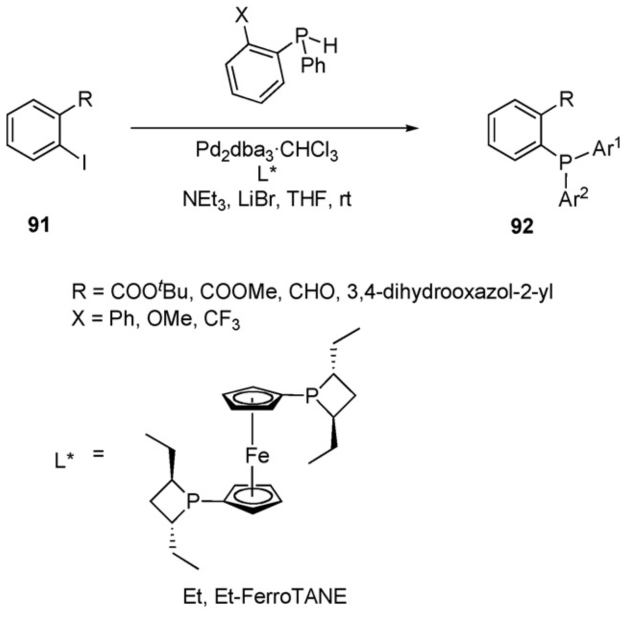
Further work of this group has used very recently a Pt complex [139] to prepare a variety of diphosphines, whereas in parallel Bergman, Toste and co-workers [143] have reported similar studies with ruthenium complexes.

Helmchen's group has further developed [144] the C–P cross-coupling reactions catalyzed by palladium. In previous work, this group [145] had synthesised some *P*-stereogenic phosphinooxazoline (PHOX) ligands, bearing both carbon and phosphorus as stereogenic elements. Their stereoselective preparation was accomplished via substrate-controlled diastereoselection, because the oxazoline moiety was enantiopure. By this method, however, only the major diastereomers were reasonably accessible and it was not applicable when the oxazoline group was not chiral.

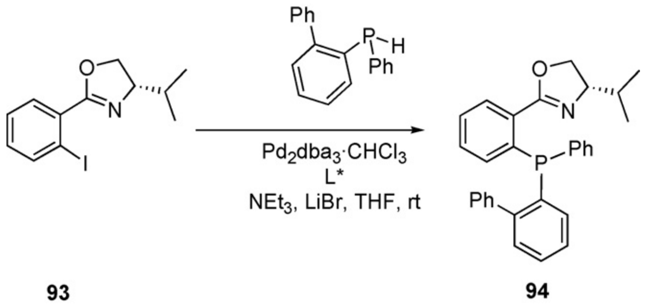
For these reasons, Pd-catalyzed cross-coupling was explored with **91**-type substrates. The substrates and conditions used are shown in Equation 15.

The effects of the base, the additive (LiBr or Bu_4NBr) and the R and X groups on enantioselectivity were investigated. Good yields and enantioselectivity (up to 93%) were found. The absolute configuration of some of the phosphines was determined by crystal structure analysis of **92** or the sulfide derivative.

Further work by the same group (Equation 16) [144] investigated the double asymmetric induction controlled by the catalyst and the preformed stereogenic centre in **93**.



Equation 15. Pd-catalyzed, cross-coupling reaction.



Equation 16. Double asymmetric induction in the synthesis of *P*-stereogenic phosphines.

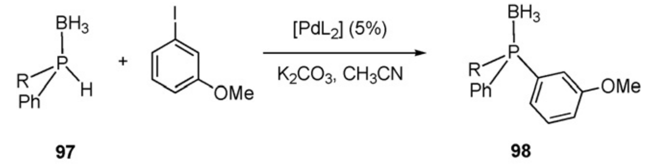
By changing the absolute configuration of the Et,Et-FerroTANE ligand the absolute configuration of the resulting phosphine **94** was inverted, which demonstrated that catalyst control dominates substrate control.

Further work of the Glueck group [138] looked recently at the catalytic, asymmetric synthesis of phosphine–boranes. The first efforts were devoted to the stereoselective synthesis of PAMP·BH_3.

The proposed catalytic cycle for such a reaction is shown in Scheme 28.

Both the Imamoto [91] and Livinghouse [38] groups reported that a loss of P stereochemistry is possible during the formation of PAMP·BH_3 (**11**) from enantiopure **95**, presumably because the anion **96** racemizes before the Pd–P bond formation. When this racemization occurs quicker than Pd–P bond formation with a chiral Pd catalyst, and if one enantiomer of the anion reacts quicker with **D** than the other, as depicted in Scheme 28, a dynamic, kinetic resolution might produce enantioenriched PAMP·BH_3 (**11**) via the mechanism shown.

Following this idea, Glueck's group screened [138] a range of commonly used chiral diphosphines (CHIRAPHOS, DUPHOS, Tol-BINAP and ^{t}Bu-Josiphos) to evaluate their activity and stereoselectivity. It was found that the palladium complex **D** with ^{t}Bu-Josiphos was a robust catalyst, although the reaction was slow and stereoselectivity was low (<10% e.e.). Studies of the stoichiometric steps of the cycle led to separation, isolation and determination of the absolute configurations of the Pd phosphido-borane complexes (**A** and **A′**). In addition, detailed mechanistic information on this useful class of Pd-mediated reactions was gathered. This gave the first *direct* corroboration of long-held assumptions about the stereochemistry of reductive elimination (with retention of configuration), suggesting that the reactions of M–P and M–C bonds are similar in terms of stereochemistry.

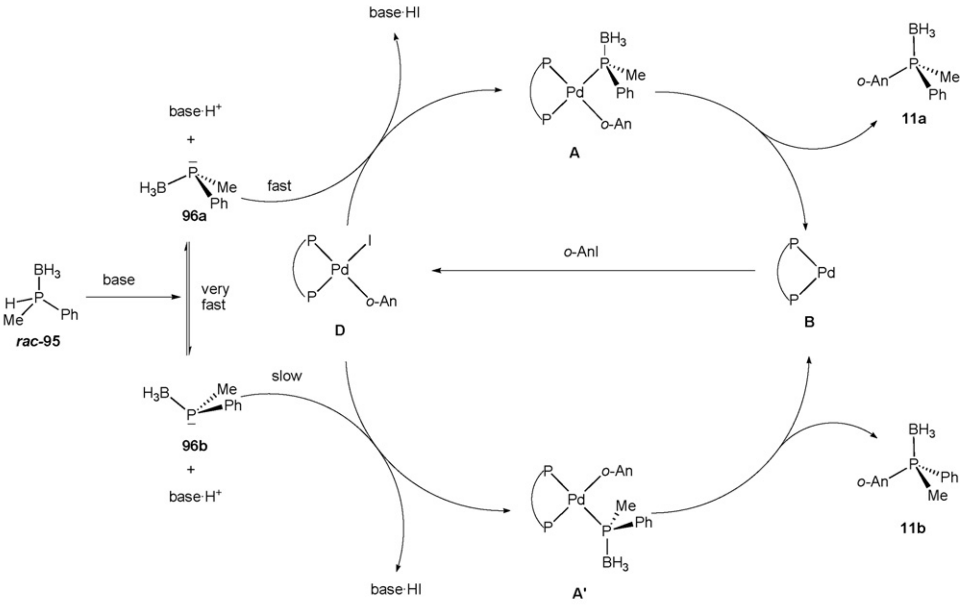


Equation 17. Pd-catalyzed cross-coupling reaction to yield a *P*-stereogenic phosphine.

This method does not have, at the moment, any direct synthetic application. Nevertheless, it has demonstrated that *P*-stereogenic phosphine–boranes can be successfully prepared via Pd-catalyzed asymmetric phosphination.

Taking up this idea, Gaumont group very recently reported [146] their preliminary results in asymmetric C–P coupling between racemic secondary phosphine–boranes, **97**, and *o*-anisyl iodide, catalyzed by several Pd/bidentate ligand systems (Equation 17).

The activity and stereoselectivity of the reaction were studied for several reaction conditions and some mechanistic studies were also performed. It was found that the nature of the R group (alkyl or aryl) exerted a great influence on stereoselectivity. The best result was obtained with R = ^{t}Bu, with 45% e.e.



Scheme 28. Proposed mechanism for asymmetric phosphination with phosphine–boranes.

6. Survey of *P*-stereogenic compounds

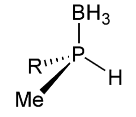
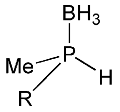
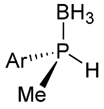
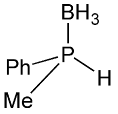
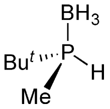
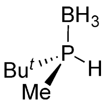
The following table is a survey of *P*-stereogenic compounds published in the last 10 years, with indication of the preparative method used. The table is organized by grouping molecules under the following criteria:

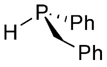
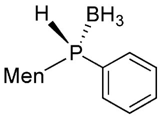
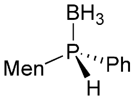
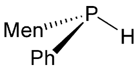
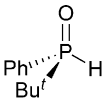
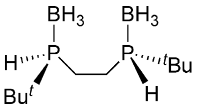
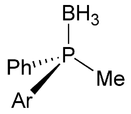
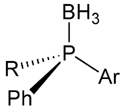
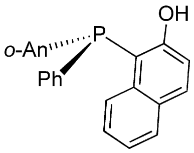
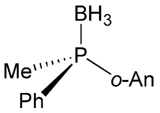
- Secondary phosphines, phosphine–boranes and oxides.
- Monodentate phosphines, phosphine–boranes and oxides.
- C_2-diphosphines and derivatives.
- C_1-diphosphines and derivatives.
- P/N and P/S potentially bidentate ligands (P = phosphine) and derivatives.
- Substances with P–X bonds (X = N, O, S or halogen).

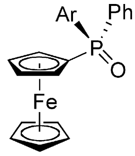
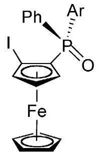
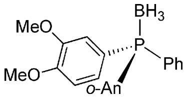
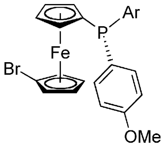
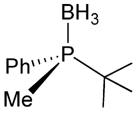
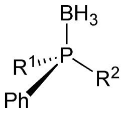
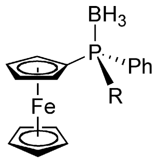
The following division is used for synthetic methods:

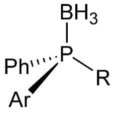
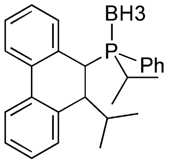
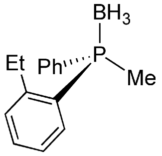
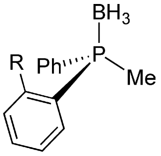
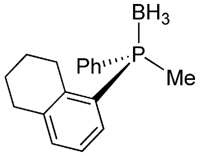
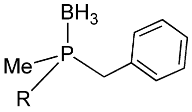
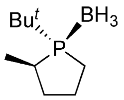
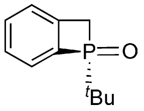
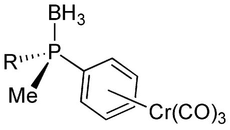
(A) Preparation by resolution of racemic or diastereomeric mixtures:
  (A1) Chemical resolution by the use of menthol and other chiral auxiliaries.
  (A2) Chemical resolution by means of cyclometallated palladium compounds.
  (A3) Direct resolution by preparative HPLC.
(B) Preparation by asymmetric synthesis:
  (B1) Use of ephedrine and other heterobifunctional auxiliaries.
  (B2) Use of sparteine for the deprotonation of dimethylphosphine–boranes and related compounds.
  (B3) Use of sparteine for the dynamic resolution of racemic phosphide-boranes.
  (B4) Use of enantiomerically pure phosphide-boranes or related compounds.
(C) Preparation by asymmetric catalysis.
(D) Preparation by miscellaneous methods.

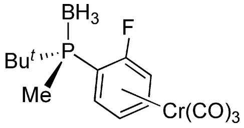
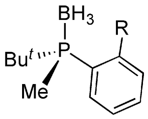
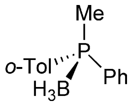
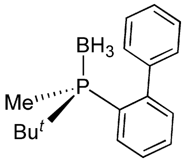
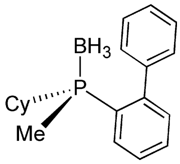
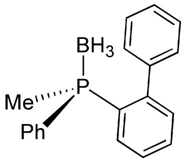
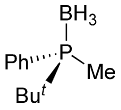
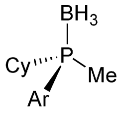
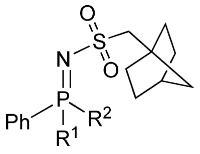
Although the table is devoted mainly to P(III) compounds, some oxides and sulfides have also been included, because they are direct precursors of free phosphines and their derivatives. In multistep preparations, only the last compound prepared is usually cited. When more than one isomer of the compound is prepared, the table usually lists only one of them. The yields refer to the last step in the synthesis and not to the overall yield. The application column usually refers to the use of the compound as a ligand in an asymmetric catalytic reaction, with no further details.

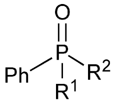
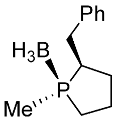
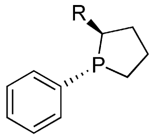
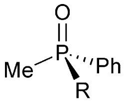
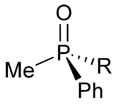
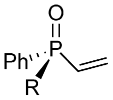
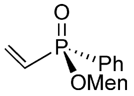
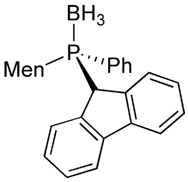
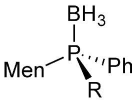
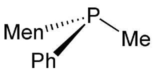
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
Secondary phosphines, phosphine-boranes or oxides					
 R = ^{t}Bu, 1-Ad	B2	79–91	87–99	Synthetic purposes	[90]
 R = Cy, ^{t}Bu, 1-Ad	A1/A3	72–97 (*S*) 75–95 (*R*)	o.p.	Synthetic purposes	[91]
 Ar = Ph, 2-^{i}PrPh, *o*-An, *o*-Tol	B2	93–99	o.p.	Synthetic purposes	[147]
	C/D	–	17	Synthetic purposes	[148]
	B2	80	o.p.	Synthetic purposes	[92]
	B1	75	95	Synthetic purposes	[149]

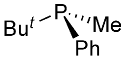
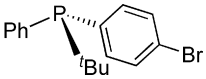
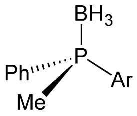
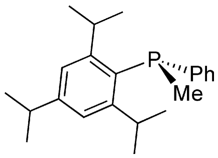
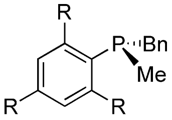
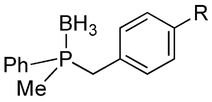
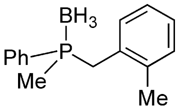
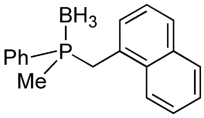
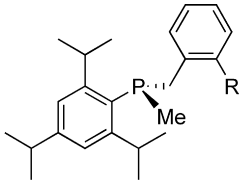
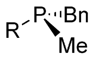
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	A2	45–63	o.p.	Synthetic purposes	[150,151]
	A1	66 (BH_3) quant. (free)	97	Synthetic purposes	[152]
	A1/D	–	o.p.	Synthetic purposes	[153]
	A1	95	13	Synthetic purposes	[154]
	B1	23–88 (crude) 75 (recr.)	18–91 (crude) o.p. (recr.)	Synthetic purposes	[155,156]
	B2	79–85	98 (crude) o.p. (recr.)	Synthetic purposes	[157]
Monodentate phosphines, phosphine-boranes or oxides					
 Ar = 1-naphthyl	B1	96 (crude) 81 (recr.)	93 (crude) o.p. (recr.)	Synthetic purposes	[54]
 R = Me, *o*-An, *o*-Tol Ar = 2-hydroxyphenyl, 2-hydroxy-1-naphthyl	B1	48–96	71-o.p.	Synthetic purposes	[42]
	B1	80	80	Synthetic purposes	[42]
	B1	–	72	Synthetic purposes	[42]

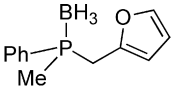
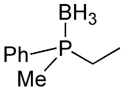
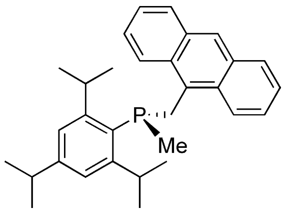
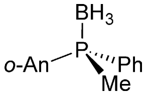
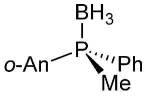
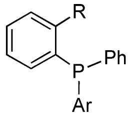
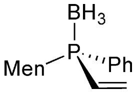
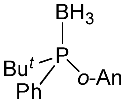
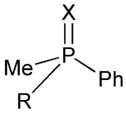
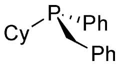
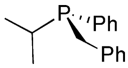
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 Ar = 1-naphth, 2-biph	B1	66 (free) 98 (oxide)	o.p. (oxide)	Synthetic purposes	[70]
 Ar = 1-naphth, 2-biph	B1	62–86	50–94	Synthetic purposes	[70]
	B1	80	o.p.	Synthetic purposes	[56]
 Ar = 1-naphth	B1	41	o.p.	Synthetic purposes	[62]
	B1	66	92 (crude) o.p. (recr.)	Synthetic purposes	[53]
 R^1 = Me, Cy, *o*-An, *o*-Tol, 1/2-naphth, 2-biph R^2 = Me, *o*-An	B1	41–99	59–99	Synthetic purposes	[73]
 R = Me, *n*-Bu, Cy, neophyl, *o*/*p*-An, *o*-Tol, 2-biph	B1	58–92 (BH_3) 83-quant. (free)	77-o.p. (BH_3) 80-o.p. (free)	Reductive coupling of alkynes and aldehydes	[60]

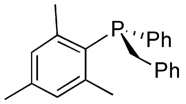
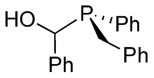
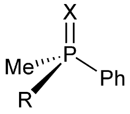
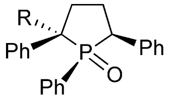
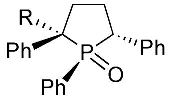
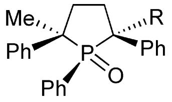
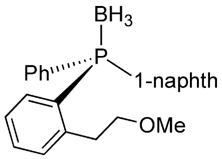
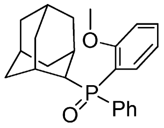
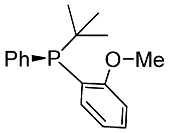
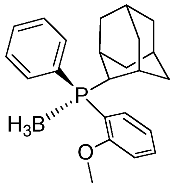
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 Ar = 1-naphth, 9-phen, 2-biph R = Me, ^{i}Pr, CH_2SiMe_3, CH_2SiPh_3	B1	31–97 (BH_3) 52–95 (free)	o.p.	Pd-hydrovinylation	[63,86]
	B1	34	0	–	[63]
	A1	91	88	Synthetic purposes	[27]
 R = Me, Et, ^{i}Pr	A1/A3	81–99	77–94	Synthetic purposes	[158]
	A1/A3	98	84	Synthetic purposes	[158]
 R = Cy, ^{t}Bu, 1-Ad	A1/A3/B4	75–93 (*S*) 80–90 (*R*)	90–98 (*S*) 91–99 (*R*)	Synthetic purposes	[91]
	B2	–	0	Synthetic purposes	[159]
	A3	52 (comb.)	o.p.	Synthetic purposes	[25]
 R = Cy, ^{t}Bu, 1-Ad	B4	81–93	75–99	Synthetic purposes	[93]

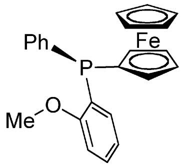
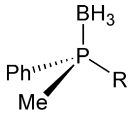
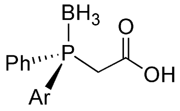
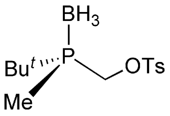
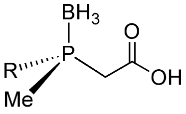
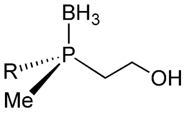
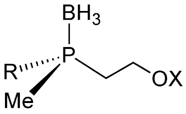
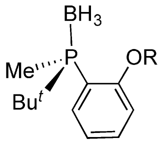
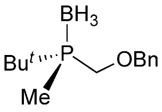
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B4	97 (BH_3, comb.) 77 (BH_3, purif., diast. pure) 90 (free)	70 (BH_3, crude) o.p. (BH_3, purif.) o.p. (free)	Synthetic purposes	[93]
 R = Me, *n*-Bu, Cy, Ph, PhS, ^{t}BuS, PhSe, CN, N_3	B4	52–91	o.p.	Synthetic purposes	[93]
	A1	92	o.p.	Synthetic purposes	[160]
	A1/A3/B4	72 (BH_3, crude) quant. (free)	75 (BH_3, crude) o.p. (BH_3, recr.) o.p. (free)	Pd-allylic substitution	[161]
	A1/D	73 (crude)	97 (BH_3, crude) o.p. (BH_3, recr.) o.p. (free)	Pd-allylic substitution	[161]
	A1	90 (crude)	94 (BH_3, crude) o.p. (BH_3, recr.) o.p. (free)	Pd-allylic substitution	[161]
	B3	88	93	Synthetic purposes	[38]
 Ar = 1-naphthyl	A1	64	o.p.	Synthetic purposes	[34]
 R^1 = Me, 1-naphth R^2 = ^{i}Pr, cyclopentyl, Cy, 1/2-naphth, 2-MeO-1-naphth, 9-phen, *p*-biph	A1	87–95 (comb. yield)	o.p. (most cases)	Synthetic purposes	[162,163]

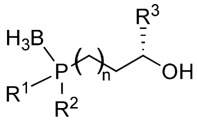
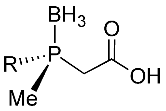
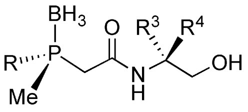
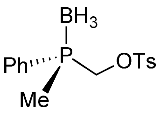
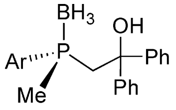
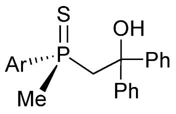
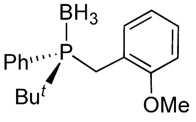
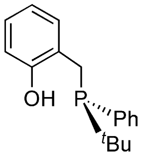
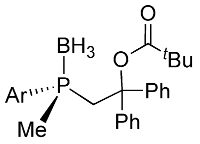
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 R^1 = Me, 1-naphth R^2 = ^{i}Pr, cyclopentyl, Cy, 1/2-naphth, 2-MeO-1-naphth, 9-phen, *p*-biph	A1	93-quant.	o.p.	Synthetic purposes	[162,163]
	A1/B2	38–53	77–91	Synthetic purposes	[164]
 R = Me, CH_2OMe, Bn	B1/D	70–82	53-o.p.	Synthetic purposes	[165]
 R = Pr, *o*-An	A1	75–95	o.p.	Synthetic purposes	[166]
 R = Pr, *o*-An	A1	70–91	o.p.	Synthetic purposes	[166]
 R = Me, Et, *o*-An	A1	72–80	92-o.p.	Synthetic purposes	[167]
	A1	72	o.p.	Synthetic purposes	[168]
	A1/D	32 (BH_3) 97 (free)	o.p.	Synthetic purposes	[153]
 R = Me, Bn	A1/B4	90–94	o.p.	Synthetic purposes	[153]
	A1/C	40–90	39–91	Synthetic purposes	[154]

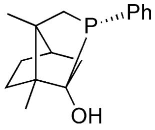
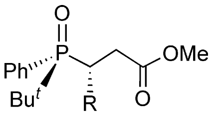
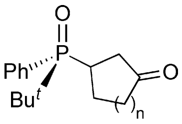
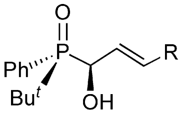
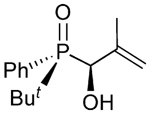
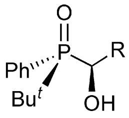
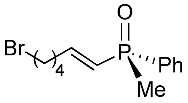
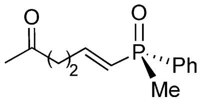
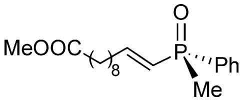
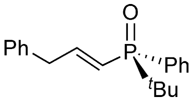
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	A2	85	o.p.	Synthetic purposes	[169]
	A2	–	o.p.	Synthetic purposes	[170]
 Ar = *o*/*p*-An, *o*-Tol, *p*-CF_3Ph, 1-naphth	B4/C	52–98	94.5-o.p.	Synthetic purposes	[142]
	C	53–90	50–73	Synthetic purposes	[136]
 R = H, Me, Ph	C	84–86	35–81	Synthetic purposes	[139]
 R = H, Me, OMe, Cl	C	80–96	41–85 (crude) 92 (recr.)	Synthetic purposes	[143]
	C	92	57	Synthetic purposes	[143]
	C	96	59	Synthetic purposes	[143]
 R = H, CN, I	C	86–88	50–70	Synthetic purposes	[139]
 R = ^{t}Bu, Cy, *o*-An, Men	C	85–93	9–56	Synthetic purposes	[139]

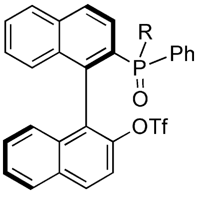
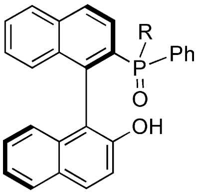
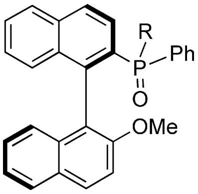
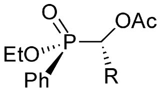
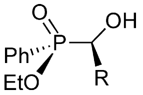
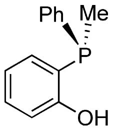
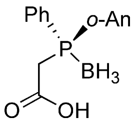
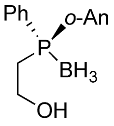
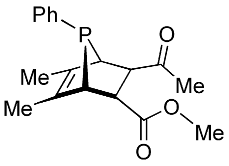
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	C	80	68	Synthetic purposes	[143]
	C	70	57	Synthetic purposes	[143]
	C	77	66	Synthetic purposes	[139]
	B4/C	–	87–93	Synthetic purposes	[137]
	B4/C	18–27	69–98	Synthetic purposes	[138]
 R = CO_2Me, $CO_2{}^tBu$, CHO, 3,4-dihydrooxazol-2-yl Ar = *o*-biph, *o*-An, *o*-CF_3Ph	C	39–79	–	Synthetic purposes	[144]
	A1	22	o.p.	Synthetic purposes	[171]
	C	quant.	0–27	Synthetic purposes	[146]
 X = O, S R = ^tBu, *o*-An, *o*-Tol, 1-naphth	A1/D	80–90	3.5–50 (oxide) 0–33 (sulfide)	Synthetic purposes	[172]
	A2	66–84	90-o.p.	Pd-hydrovinylation	[31,151,173]
	A2	52–54	o.p.	Synthetic purposes	[174]

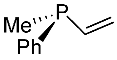
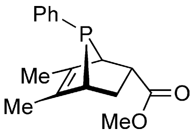
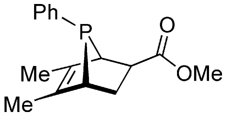
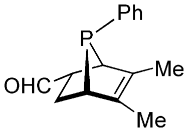
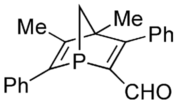
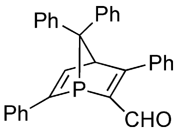
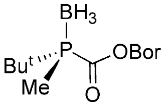
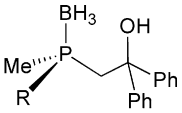
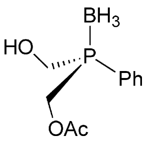
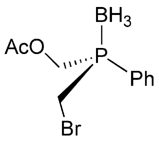
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	A2	32–86	60-o.p.	Pd-hydrovinylation	[32]
	A2	30–60	o.p.	Synthetic purposes	[175]
 X = O, S R = ^{t}Bu, *o*-An, *o*-Tol, 1-naphth	A1	–	3.5–39 (oxide) 10–33 (sulfide)	Synthetic purposes	[176]
 R = Me, Et, Bn, allyl, prenyl SPh, CH(OH)Ph, CH(OH)Cy, CH(CH$_3$)$_2$ picolyl, oxazoline	B2/D	61–93 (oxide) 76–96 (free)	80–92	Synthetic purposes	[177,178]
 R = Et, allyl, prenyl	B2/D	73–89	o.p.	Synthetic purposes	[177]
 R = COMe, CH(OH)Ph	B2/D	53–85	o.p.	Synthetic purposes	[177]
	B1	28	o.p.	Synthetic purposes	[179]
	B1	85	o.p.	Synthetic purposes	[180]
	B1	98	94	Synthetic purposes	[180]
	B1	37	94	Synthetic purposes	[180]

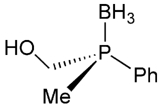
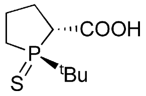
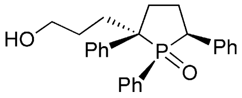
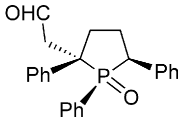
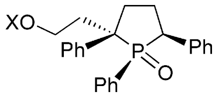
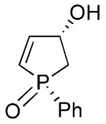
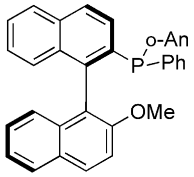
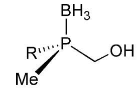
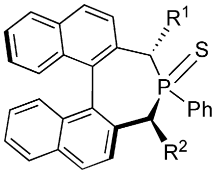
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B1	98	84	Synthetic purposes	[180]
 R = *n*-Bu, *o*-An, 1-naphth	B1	–	o.p.	Synthetic purposes	[39]
 Ar = *o*-An, *o*-Tol, 1-naphth	B1	55–60 (BH_3) 90–92 (free)	o.p.	Pd-allylic substitution	[87]
	B2	83	o.p.	Synthetic purposes	[90]
 R = ^{t}Bu, Cy, 1-Ad	B2	60–70	>90	Synthetic purposes	[81,89]
 R = ^{t}Bu, Cy, 1-Ad	B2	quant.	o.p.	Synthetic purposes	[81,89]
 R = ^{t}Bu, Cy, 1-Ad X = Ms, Ts	B2	64–96	o.p.	Synthetic purposes	[81,89]
 R = H, Me, CH_2OCH_3	A1/B4	68–70 (BH_3) 88–95 (free)	o.p.	Cu-conjugate addition	[181]
	B2	62	o.p.	Synthetic purposes	[92]

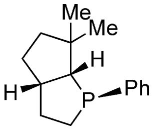
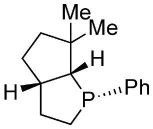
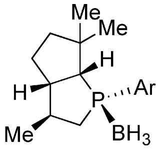
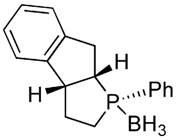
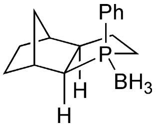
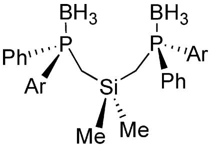
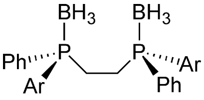
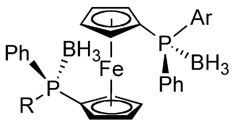
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 n = 0,1 R^1, R^2 = ^{t}Bu, Ph, *o*-An, 1-naphth R^3 = Me, Ph	B3	18 quant.	o.p.	Synthetic purposes	[182]
 R = Ph, Fc	B2	–	o.p.	Synthetic purposes	[183]
 R = ^{t}Bu, 1-Ad, Ph, Fc	B2	–	o.p.	Synthetic purposes	[183]
	B2	75	o.p.	Synthetic purposes	[184]
 Ar = Ph, *o*-An, *o*-Tol, 1-naphth	B2	81–88	79–87	Synthetic purposes	[77]
 Ar = Ph, *o*-An, *o*-Tol, 1-naphth	B2	79–94	60–79	Synthetic purposes	[77]
	B3	63–80	95-o.p.	Synthetic purposes	[38,185]
	B3	96	94.3	Sn-complex	[185]
 Ar = Ph, 2-^{i}PrPh, *o*-An, *o*-Tol	B2	46–76 (recr.)	75-o.p. (crude) o.p. (recr.)	Synthetic purposes	[147]

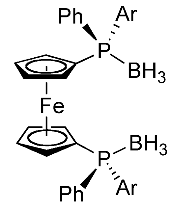
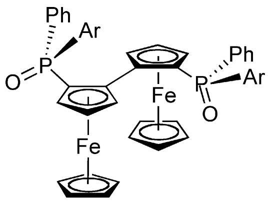
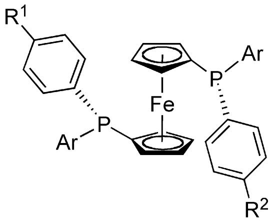
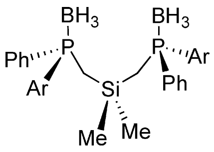
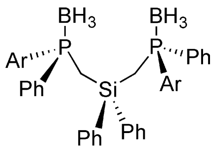
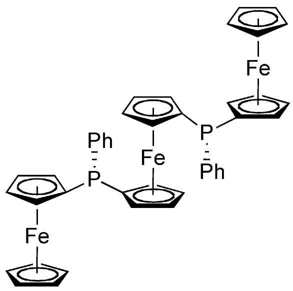
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	D	83	o.p.	Synthetic purposes	[186]
 R = H, Me, Ph	B4	63–78	54–82	Synthetic purposes	[187,188]
 n = 1, 2	B4	78–81	96	Synthetic purposes	[187,188]
 R = H, Me, Ph	B4	63–77	58–60	Synthetic purposes	[187,188]
	B4	77.2	74	Synthetic purposes	[187,188]
 R = Me, ^{s}Bu, ^{t}Bu, Cy, Ph, 1/2-naphth, 2-thienyl, 2-furyl, 2-pyridyl	B4	44–80	44-o. p	Synthetic purposes	[187,188]
	D	86	o.p.	Synthetic purposes	[188,189]
	D	85	o.p.	Synthetic purposes	[188,189]
	D	74	o.p.	Synthetic purposes	[188,189]
	D	72	o.p.	Synthetic purposes	[188,189]

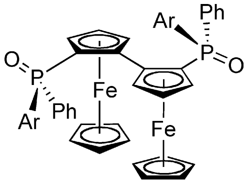
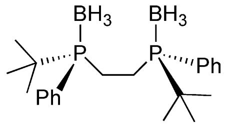
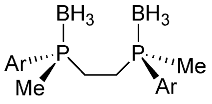
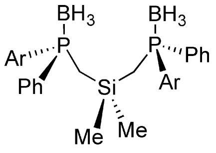
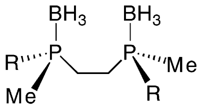
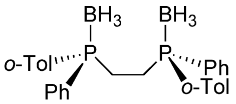
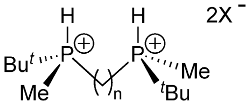
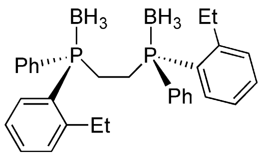
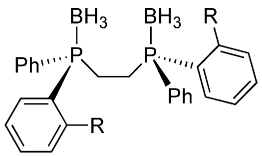
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 R = Me, *o*-An	D	45–79 (comb.)	o.p.	Synthetic purposes	[190]
 R = Me, *o*-An	D	86–92	o.p.	Synthetic purposes	[190]
 R = Me, *o*-An	D	76–81 (oxide) 36–83 (free)	o.p. (oxide) 0-o.p. (free)	Synthetic purposes	[190]
	C/D	–	o.p.	Synthetic purposes	[191]
	C/D	–	2-o.p.	Synthetic purposes	[191]
	D	81	o.p.	Synthetic purposes	[192]
	–	86	o.p.	Synthetic purposes	[193]
	–	76	o.p.	Synthetic purposes	[193]
	A2/D	80	o.p.	Synthetic purposes	[21,107]

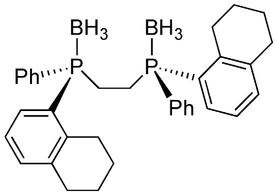
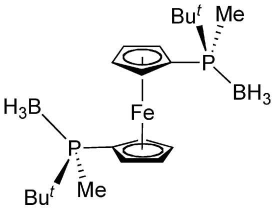
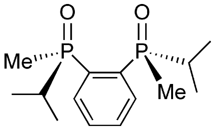
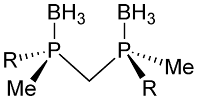
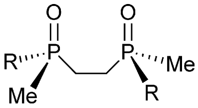
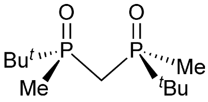
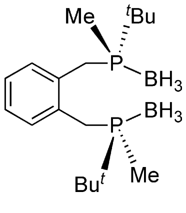
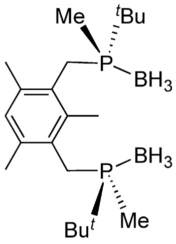
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	A2/D	87	o.p.	Synthetic purposes	[21,119]
	A2/D	75	o.p.	Synthetic purposes	[21,100]
	A2/D	80	o.p.	Synthetic purposes	[21,100]
	A2/D	97	o.p.	Synthetic purposes	[124]
	A1	88	o.p.	Synthetic purposes	[194]
	A1	45	o.p.	Synthetic purposes	[194]
	A1/B1	32	95	Synthetic purposes	[149]
 R = Cy, ^{t}Bu, Ph	B2	16–94	0–92	Synthetic purposes	[195,196]
	B2/D	22–54	19–92	Synthetic purposes	[197]
	B2/D	44	90	Synthetic purposes	[197]

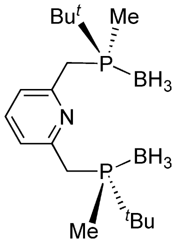
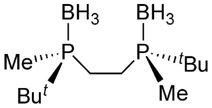
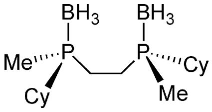
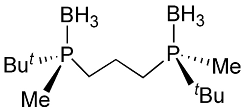
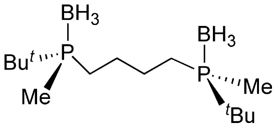
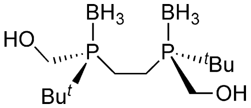
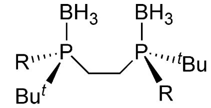
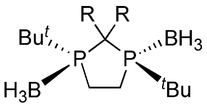
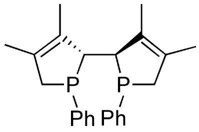
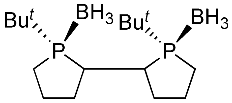
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B2/D	82	90	Synthetic purposes	[197]
	B2	40 (recr.)	72 (crude) o.p. (recr.)	Synthetic purposes	[198]
	B2/D	73 (oxide) 81 (free)	o.p.	Synthetic purposes	[177]
	B2/D	75	o.p.	Synthetic purposes	[177]
 X = H, Ms	B2/D	74–93	o.p.	Synthetic purposes	[177]
	B2/D	0–78	0–52	Synthetic purposes	[199]
	D	21–25	o.p.	Synthetic purposes	[200]
 R = Cy, ^{t}Bu, 1-Ad, Ph	B2	70–74	75–93 99 (R = 1-Ad, recr.)	Synthetic purposes	[90]
 R^1, R^2 = Me, Et, ^{i}Pr, Bn, $SiMe_3$	B2/D	35–96 (sulfide) 70–85 (free)	o.p.	Rh-hydrogenation Rh-hydroboration Pd-Suzuki coupling	[201]

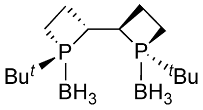
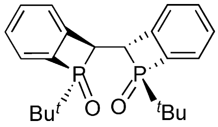
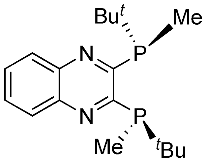
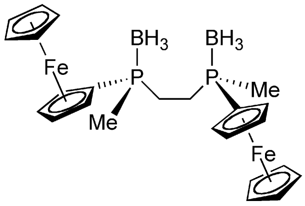
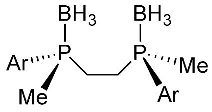
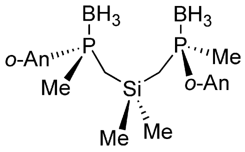
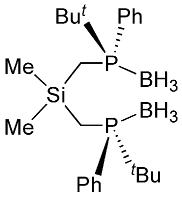
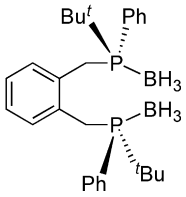
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	D	7	o.p.	Acyl transfer	[202]
	D	53	o.p.	Acyl transfer	[202,203]
 Ar = Ph, 3,5-di(^{t}Bu)Ph	D	85 (comb.)	99.7	Kinetic resolution of alcohols	[202,203]
	A3/D	44 (BH_3, comb.) 78 (BH_3, diast. pure)	o.p.	Anhydride activation Kinetic resolution of alcohols	[204]
	A3/D	15–35 (BH_3, comb.)	o.p.	Anhydride activation Kinetic resolution of alcohols	[204]
C_2-diphosphines and derivatives					
 Ar = 1-naphthyl	B1	98 (BH_3) 78 (free)	o.p. (BH_3) o.p. (free)	Rh-hydrogenation Ru-hydrogenation Pd-allylic substitution	[54]
 Ar = 1-naphthyl	B1	66 (BH_3) 94 (free)	o.p. (BH_3) o.p. (free)	Ru-cyclopropanation Ru-epoxidation	[84]
 Ar = *o*-An, 1/2-naphth, 9-phen, 2-biph	B1	72–81 (free)	o.p. (free)	Rh-hydrogenation	[55]

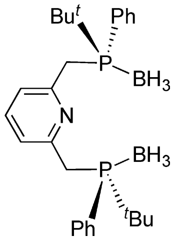
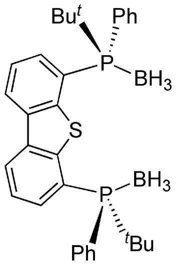
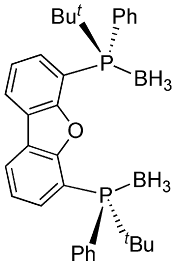
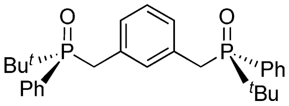
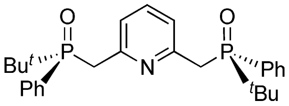
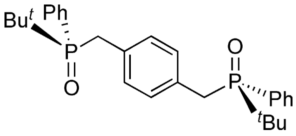
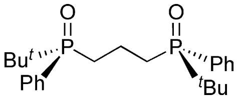
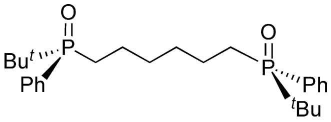
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 Ar = *o*-An, 1-naphth	B1	48–72 (BH_3) 76–86 (free)	o.p. (free)	Rh-hydrogenation	[69]
 Ar = 1-naphth, 2-biph	B1	58–70 (oxide) 40–44 (free)	o.p. (free, purif.)	Synthetic purposes	[70]
 Ar = 1-naphth R^1, R^2 = CF_3, OMe	B1	36–70	>90 (crude) o.p. (purif.)	Rh-hydroformylation	[62]
 Ar = *o*-An	B1	85	o.p.	Pd-allylic substitution	[82]
 Ar = *o*-Tol	B1	80	o.p.	Rh-hydrogenation	[82]
	B1	54	o.p.	Pd-allylic substitution	[61]

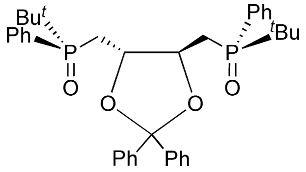
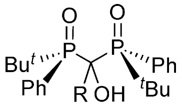
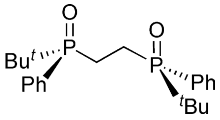
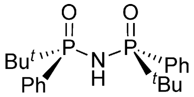
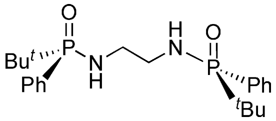
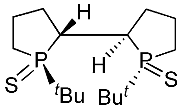
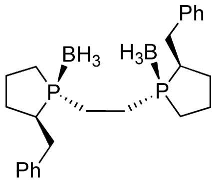
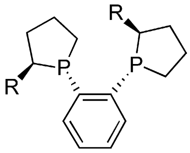
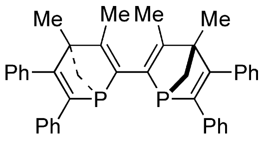
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B1	35 (oxide) 38 (free)	o.p. (oxide) o.p. (free)	Pd-allylic substitution	[61]
	B1	44 (BH_3) 93 (free)	o.p. (BH_3) o.p. (free)	Synthetic purposes	[53]
 Ar = Mes, 9-anthrhyl	B2	39–62 (BH_3) 86–88 (free)	18–37 (BH_3) 18–37 (free)	Synthetic purposes	[53]
 Ar = *o*-An	B1	75.5 (BH_3) 21 (free)	o.p. (BH_3) o.p. (free)	Ru-hydrogenation	[85]
 R = ^{i}Pr, ^{t}Bu, CEt$_3$, 1-Ad, cyclopentyl, Cy, 1-MeCy	B2	30–69	75-o.p.	Rh-hydrogenation Ru-hydrogenation Rh-hydrosilylation Ir-hydrogenation	[35,205–215]
	A1	66 (BH_3) 96 (free)	o.p.	Rh-hydrogenation	[160]
 n = 1,2 X = BF$_4$, OTf	B2	91	o.p.	Rh-hydrogenation	[216]
	A1	quant. (free)	o.p.	Rh-hydrogenation	[27,207]
 R = Me, Et, ^{i}Pr	A1/A3	57–79 (BH_3) quant. (free)	o.p.	Rh-hydrogenation	[158]

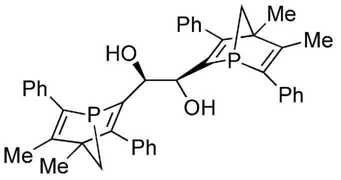
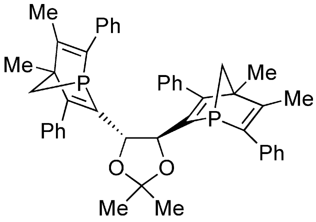
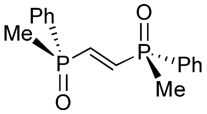
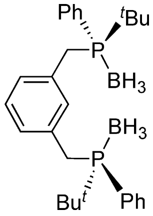
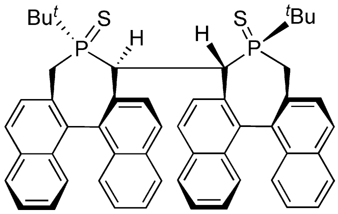
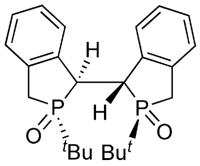
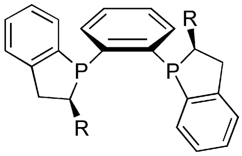
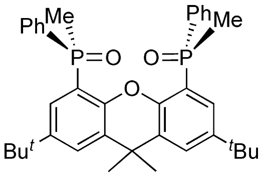
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	A1/A3	55 (BH_3) quant. (free)	o.p.	Rh-hydrogenation	[158]
	A3	50 (BH_3, *rac*) quant. (free)	o.p.	Rh-hydrosilylation	[88]
	A2	11 (oxide, *rac*) 85 (free)	99 (oxide) 97 (free)	Rh-hydrogenation	[217]
 R = ^{i}Pr, Cy, ^{t}Bu, Ad, Ph	B2	7–28 (BH_3) quant. (free)	o.p.	Rh-hydrogenation Rh-hydrosilylation Cu-conjugate addition	[80,207–210,213,214,218]
 R = ^{t}Bu, 1-Ad	B2	–	o.p.	Fe-Diels–Alder	[219]
	B2	–	o.p.	Fe-Diels–Alder	[219]
	A1/A3/B4	30–68 (BH_3) quant. (free)	o.p.	Rh-hydrogenation	[36,91]
	A1/A3/B4	35	98	Synthetic purposes	[91]

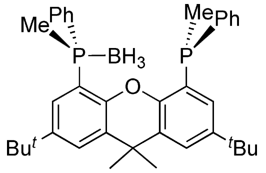
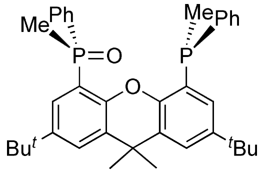
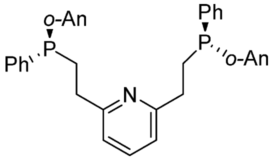
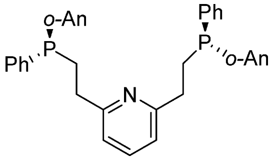
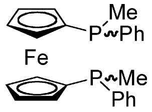
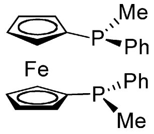
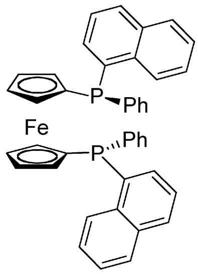
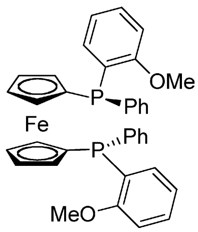
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	A1/A3/B4	84	99	Synthetic purposes	[91]
	A1/A3/B4	60	99	Synthetic purposes	[91]
	A1/A3/B4	58	–	Synthetic purposes	[91]
	A1/A3/B4	69	98	Synthetic purposes	[91]
	A1/A3/B4	80	–	Synthetic purposes	[91]
	B2	50	o.p.	Synthetic purposes	[157]
 R = Me, Bn, CH_2COOMe	B2/B4	46 quant.	o.p. (crude) o.p. (recr.)	Synthetic purposes	[157]
 R = H, Me	B2/B4	35–53	o.p.	Synthetic purposes	[157]
	A2	67–90	o.p.	Rh-hydrogenation Au-complex	[220,221]
	B2	quant.	0	Synthetic purposes	[159]

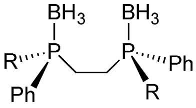
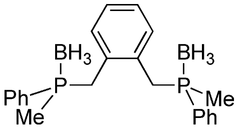
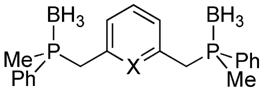
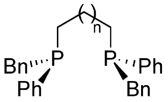
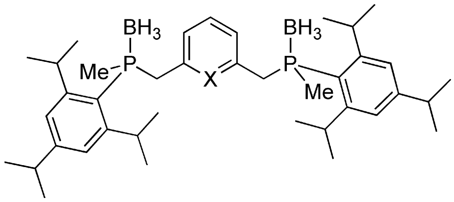
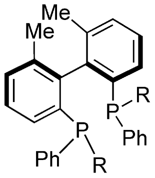
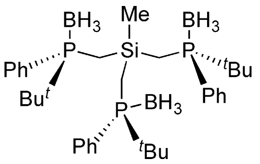
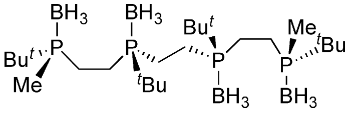
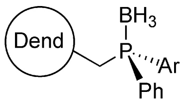
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B2	24 (crude, BH_3) 15 (recr., BH_3) 83 (free)	94.7 (crude) o.p. (recr.)	Rh-hydrogenation	[222]
	A1/A3	44	98.8-o.p.	Rh-hydrogenation	[25]
	B2/B4	80	o.p.	Rh-hydrogenation Rh-hydrosilylation Rh-addition of arylboronic acids Pd-ring opening	[92,213]
	B2	25–35 (BH_3, recr.) 78 (free)	o.p.	Rh-hydrogenation Pd-allylic substitution	[37]
 Ar = Ph, *o*-An, *o*-Tol, 1-naphth	B2	67–72 (BH_3) 91-quant. (free)	96–99 (BH_3)	Synthetic purposes	[77]
	B2	73 (BH_3) 81 (free)	o.p.	Synthetic purposes	[77]
	B3	67	–	Synthetic purposes	[38]
	B3	68	o.p.	Synthetic purposes	[38]

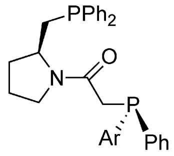
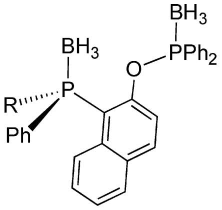
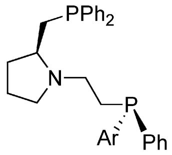
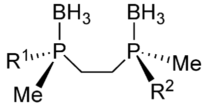
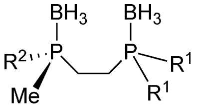
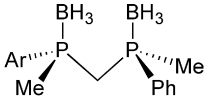
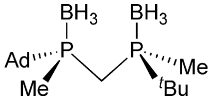
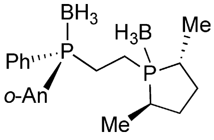
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B3	71	o.p.	Synthetic purposes	[38]
	B3	76	o.p.	Synthetic purposes	[38]
	B3	75	o.p.	Synthetic purposes	[38]
	B4	88	o.p.	Synthetic purposes	[223]
	B4	73	o.p.	Synthetic purposes	[223]
	B4	19	o.p.	Synthetic purposes	[223]
	B4	70	o.p.	Synthetic purposes	[223]
	B4	83	o.p.	Synthetic purposes	[223]

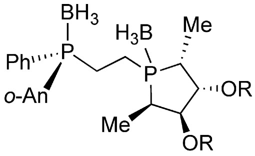
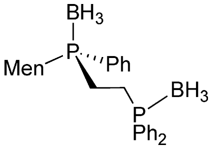
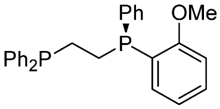
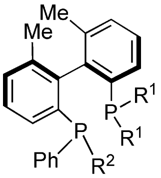
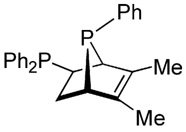
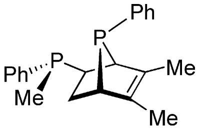
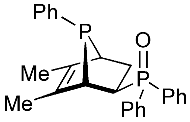
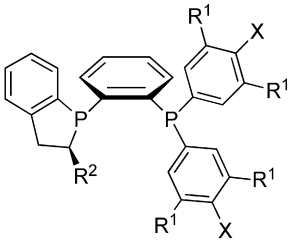
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B4	83	o.p.	Synthetic purposes	[223]
 R = Me, Ph	B4	73–80	o.p.	Synthetic purposes	[223]
	B4/D	78 (comb.)	o.p.	Synthetic purposes	[223]
	B4	63 (BH_3)	o.p.	Synthetic purposes	[223]
		74 (free)			
	B4	74	o.p.	Synthetic purposes	[223]
	B2	20 (sulfide) 88 (free)	o.p.	Rh-hydrogenation Ru-hydrogenation	[224–226]
	A1/B2	41 (recr., BH_3) 89–91 (free)	96 (crude) o.p. (recr.)	Rh-hydrogenation	[164,227]
 R = Me, Bn	B1/D	52–78	60-o.p.	Rh-hydrogenation	[165]
	A2	85	o.p.	Pd-allylic substitution Rh-hydrogenation Ru-hydrogenation Rh-isomerization	[228,229]

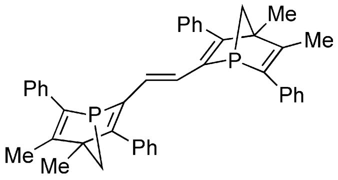
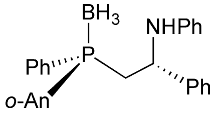
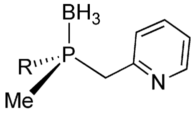
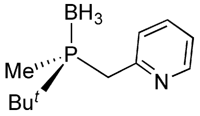
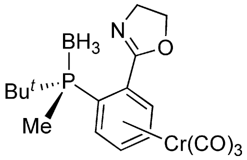
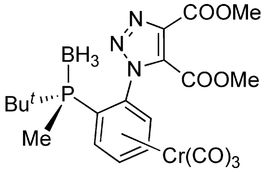
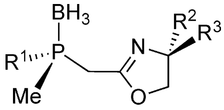
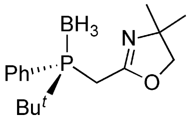
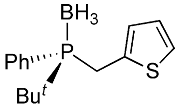
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	A1/D	70	o.p.	Pd-allylic substitution Rh-hydrogenation Ru-hydrogenation Ir-hydrogenaiton	[230]
	A1/D	50	o.p.	Pd-allylic substitution Rh-hydrogenation Ru-hydrogenation Ir-hydrogenaiton	[230]
	D	85	o.p.	Synthetic purposes	[188,189]
	B3	54	98.5 (crude) o.p. (recr.)	Crystallographic investigation	[95]
	D	25 (sulfide) 90 (free)	o.p.	Rh-hydrogenation	[231]
	A1	30–34 (oxide) 89 (free)	o.p.	Rh-hydrogenation	[232]
 R = Me, ^{i}Pr	D	–	o.p.	Ru-hydrogenation Rh-hydrogenation	[233]
	A1/D	37–39	99.4–99.6	Pd-allylic substitution	[234]

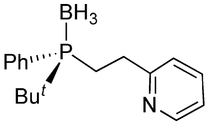
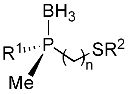
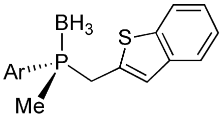
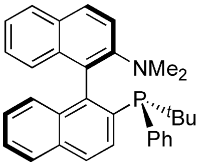
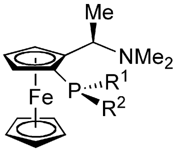
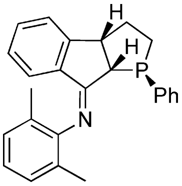
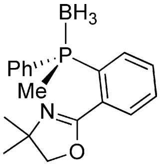
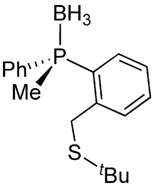
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	A1/D	–	o.p.	Pd-allylic substitution	[234]
	A1/D	–	o.p.	Pd-allylic substitution	[234]
	B1	–	o.p.	Pd-allylic substitution	[235]
	B1	–	o.p.	Pd-allylic substitution	[235]
	B1	10	5	Synthetic purposes	[58]
	B1	34	85	Synthetic purposes	[58]
	B1	–	o.p.	Pd-allylic substitution	[71]
	B1	–	o.p.	Pd-allylic substitution	[71]

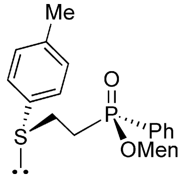
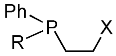
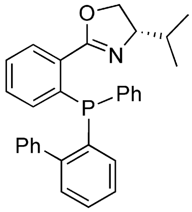
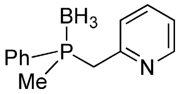
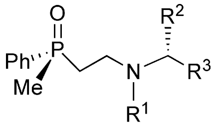
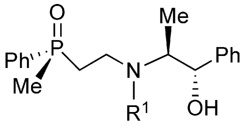
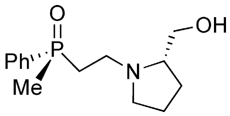
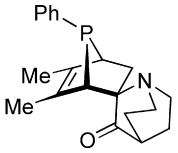
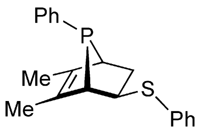
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 Ar = *o*-An, 1-naphth	B1	–	o.p.	Synthetic purposes	[39]
	C	87	74	Synthetic purposes	[143]
 X = CH, N	C	86–89	84–95	Synthetic purposes	[143]
 n = 0, 1	C	81–87	47–93	Synthetic purposes	[139]
 X = CH, N	C	86–90	17–72	Synthetic purposes	[139]
 R = Cy, ^{t}Bu	D	–	–	Synthetic purposes	[236]
	A3	65 (BH_3) 67 (free)	o.p.	Synthetic purposes, Rh-complex	[26]
	B2/B4	65 (BH_3) 95 (free)	o.p.	Rh-hydrogenation	[94]
 Dend: carbosilane dendrimer Ar = 2-biph, 9-phen	B1	15–56 (free)	o.p.	Pd-hydrovinylation	[86]

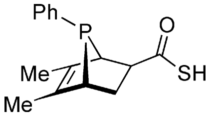
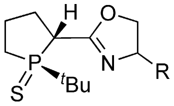
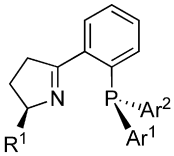
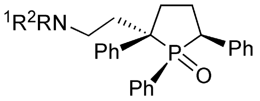
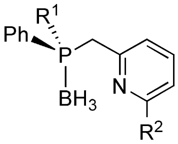
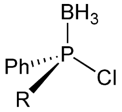
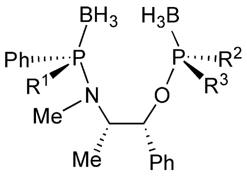
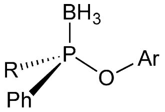
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
C_1-diphosphines and derivatives					
 Ar = *o*-An, *o*-Tol, 1-naphth	B1	48–51	o.p.	Pd-allylic substitution	[87]
 R = Me, *o*-An	B1	25–54 (BH_3) 80–85 (free)	–	Synthetic purposes	[42]
 Ar = *o*-An, *o*-Tol, 1-naphth	B1	58–60	o.p.	Pd-allylic substitution	[87]
 R^1 = ^{t}Bu, Cy, 1-Ad, Ph R^2 = ^{t}Bu, Cy, 1-Ad	B2/B4	10 quant.	o.p.	Rh-hydrogenation	[81,89,237,238]
 R^1 = Cy, Ph R^2 = 1-Ad	B2/B4	63–70	o.p.	Rh-hydrogenation	[81,89]
 Ar = mesityl	B2	66 (BH_3) 82 (free)	82–86 (BH_3) 82–86 (free)	Synthetic purposes	[53]
	B2/B4	20 (BH_3) quant. (free)	o.p.	Cu-conjugate addition	[218]
	A3	45 (comb.)	o.p.	Rh-hydrogenation	[239]

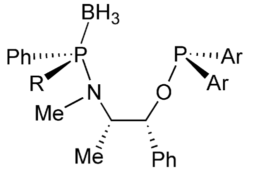
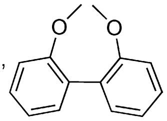
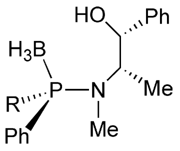
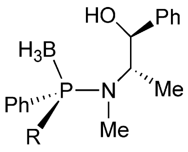
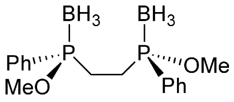
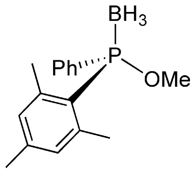
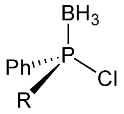
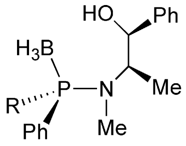
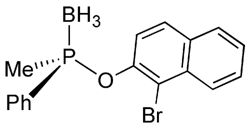
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 R = H, Me	A3	24–30 (comb.)	o.p.	Rh-hydrogenation	[239]
	A1	91 (BH_3) quant. (free)	o.p.	NMR investigation	[171]
	B1	–	70	Synthetic purposes	[240]
 R^1 = Ph,*o*-Tol R^2 = Cy, ^{t}Bu	D	–	–	Synthetic purposes	[236]
	A2/D	quant.	o.p.	Synthetic purposes	[21,241]
	A2/D	70–100	o.p.	Synthetic purposes	[21,118,119]
	A2/D	54	o.p.	Synthetic purposes	[21,242]
 R^1 = H, ^{t}Bu R^2 = Me, ^{i}Pr X = H, OMe	D	–	o.p.	Ru-hydrogenation Rh-hydrogenation	[233]

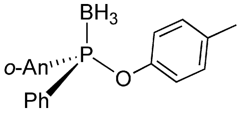
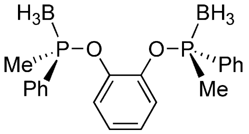
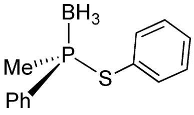
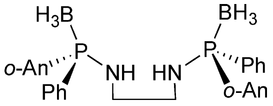
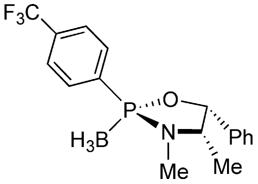
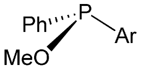
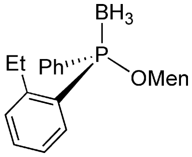
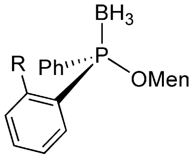
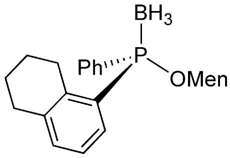
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	A1/D	50	o.p.	Synthetic purposes	[230]
P/N and P/S potentially bidentate ligands (P = phosphine) and derivatives					
	B1	76	96	Synthetic purposes	[83]
 R = 1-Ad	B2/B4	72	99	Synthetic purposes	[90]
	A1/A3/B4	85	96	Synthetic purposes	[91]
	B4	42	o.p.	Synthetic purposes	[93]
	B4	66	o.p.	Synthetic purposes	[93]
 R^1 = ^{t}Bu, 1-Ad, Ph, Fc R^2 = H, Me, ^{i}Pr R^3 = H, ^{i}Pr, ^{t}Bu	B2	–	o.p.	Pd-allylic substitution	[183]
	B3	90	>82	Synthetic purposes	[38]
	B3	85	95	Synthetic purposes	[38]

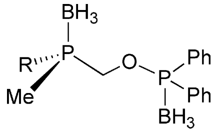
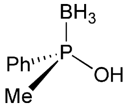
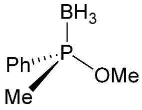
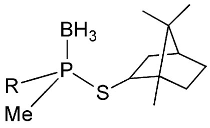
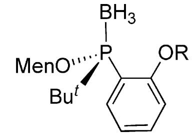
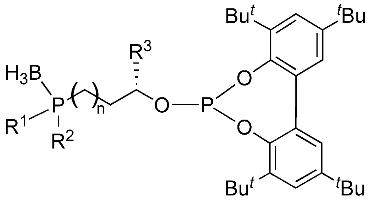
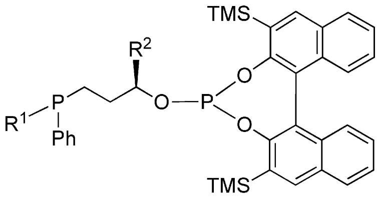
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B3	90	92	Synthetic purposes	[38]
 n = 1,2 R^1 = ^{t}Bu, Ph R^2 = Bn, Cy, ^{t}Bu,1-Ad, Ph, *o*/*p*-Tol, *p*-NO_2-Ph, 2-naphth	B2	69–98	o.p.	Pd-allylic substitution	[184]
 Ar = Ph, 2-^{i}PrPh, *o*-An, *o*-Tol	B2/B4	71–94 (recr.)	o.p.	Synthetic purposes	[147]
	D	23	o.p.	Pd-enolate vinylation	[243]
 R^1 = Cy, ^{t}Bu, Ph, 1-Naphth R^2 = Me, Cy, Ph, *o*-An, 1/2-Naphth, 2-biph	D	78–91	o.p.	Rh-hydrogenation	[244]
	D	–	o.p.	Pd-allylic substitution Rh-hydrogenation Ru-hydrogenation Ir-hydrogenation	[245,246]
	B4/C	68	o.p.	Synthetic purposes	[142]
	B4/C	62	o.p.	Synthetic purposes	[142]

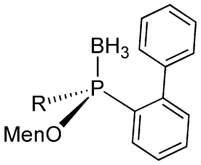
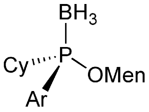
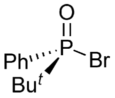
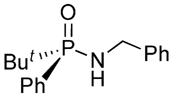
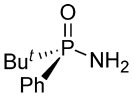
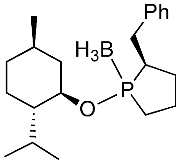
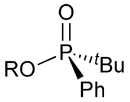
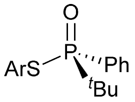
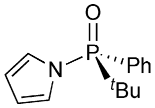
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	A1	21	o.p.	Synthetic purposes	[168]
 X = CN, $CO_2{}^tBu$ R = Me, ^{i}Bu, Cy, *o*-An, Mes, 2,4,6-triisopropylphenyl	C	60–100 (selectivity)	0–22	Synthetic purposes	[135]
	C	50–86	50–86	Synthetic purposes	[144]
	C	94	48	Synthetic purposes	[143]
 R^1, R^2 = H, Me R^3 = ^{i}Pr, Ph, CH_2OH, CH_2OMe	A1	93–98 (oxide) 70–80 (free)	o.p.	Ru-hydrogen transfer	[167]
 R^1 = H, Me	A1	87–95 (oxide) 70–80 (free)	o.p.	Ru-hydrogen transfer	[167]
	A1	92	o.p.	Synthetic purposes	[167]
	A2/D	70	o.p.	Synthetic purposes	[21,108]
	A2/D	–	o.p.	Anti-cancer studies	[21,125]

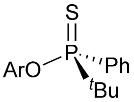
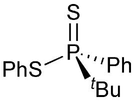
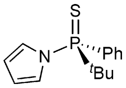
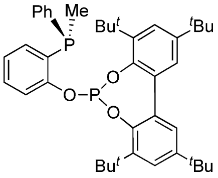
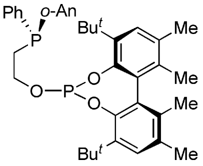
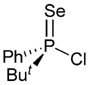
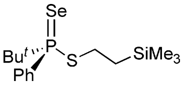
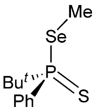
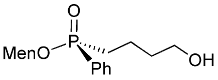
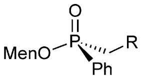
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	A2/D	50	o.p.	Synthetic purposes	[21,100]
	B2	70–80 (sulfide) 50–70 (free)	o.p.	Rh-hydrogenation	[198]
 R^1 = Me, ^{i}Pr, ^{t}Bu, Ph Ar^1 = 2-biph, 1-naphth Ar^2 = Ph, 3,5-$(CF_3)_2C_6H_3$	D	6–51	o.p.	Synthetic purposes	[145]
 R^1 = H, Et R^2 = Et, Bn	B2/D	23–40 (oxide) 44–79 (free)	o.p.	Synthetic purposes	[177]
 R^1 = Me, *o*-An R^2 = H, Me	B1	85–96	o.p.	Rh-complex	[57]
Substances with P–X bonds (X = N, O, S or halogen)					
 R = Me, *o*-An, *o*-Tol	B1	–	–	Synthetic purposes	[41,42,53]
 R^1 = Me, ^{t}Bu, Ph, *o*-An, 1/2-naphth R^2 = Cy, Ph R^3 = Me, Cy, Ph, *o*-An	B1	18–79 (BH_3) 70–90 (free)	–	Rh-hydrogenation	[41,82]
 R = Me, *o*-An, *o*-Tol Ar = 2-bromophenyl, 1-bromo-2-naphthyl	B1	66–73	71-o.p.	Synthetic purposes	[42]

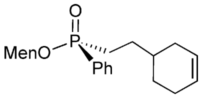
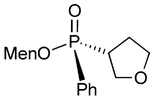
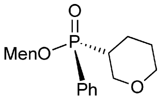
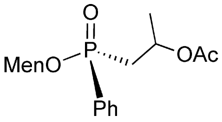
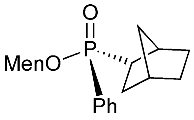
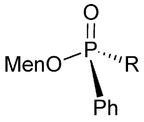
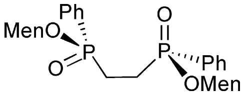
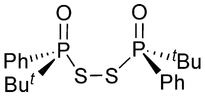
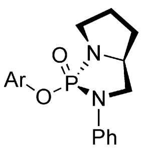
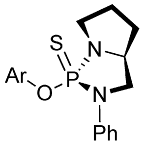
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 R = Me, *n*-Bu, Ph, 1-naphth Ar = Ph, *p*-Tol, 3,5-$(CF_3)_2C_6H_3$, 	B1	76–96 (BH_3) 62–96 (free)	≥95 (BH_3) ≥92 (free)	Rh-hydroformylation	[59,74]
 R = ^{t}Bu, *o*-An	B1	93	o.p.	Synthetic purposes	[56]
 R = ^{t}Bu, *o*-An	B1	94–97	o.p.	Synthetic purposes	[56]
	B1	88	o.p.	Pd-allylic substitution	[82]
	B1	55	o.p.	Synthetic purposes	[53]
 R = Me, Cy, *o*-An, *o*-Tol, 1/2-naphth, 2-biph	B1	45–99	85–99 (BH_3, crude) 59–95 (BH_3, purif.) 0 (R = 1-naphth)	Synthetic purposes	[72,73]
 R = Me, Cy, ^{t}Bu, *o*-An, *o*-Tol, 1/2-naphth, 1-biph	B1	81–95 (BH_3) 91 (free)	o.p.	Synthetic purposes	[72,73]
	B1	66	91	Synthetic purposes	[73]

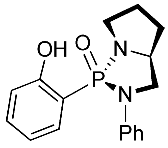
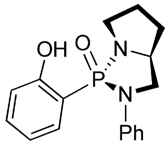
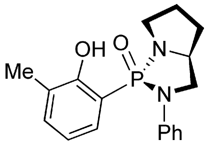
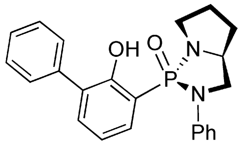
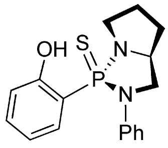
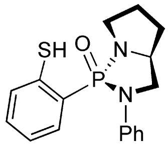
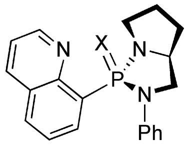
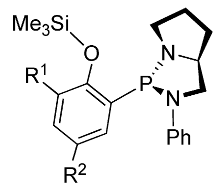
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B1	85	97	Synthetic purposes	[73]
	B1	86	–	Synthetic purposes	[73]
	B1	87	60	Synthetic purposes	[73]
	B1	89	96	Synthetic purposes	[73]
	B1	–	o.p.	Crystallographic investigation	[66]
 Ar = 2-biph	B1	60	o.p.	Pd-hydrovinylation	[63]
	A1	70	o.p.	Synthetic purposes	[27]
 R = Me, Et, ^{i}Pr	A1/A3	70–84 (comb.)	o.p.	Synthetic purposes	[158]
	A1/A3	80 (comb.)	o.p.	Synthetic purposes	[158]

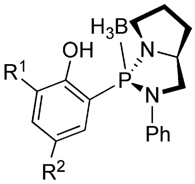
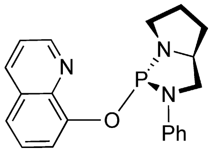
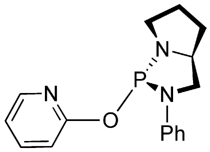
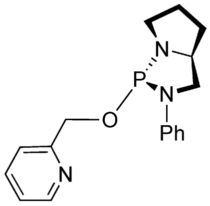
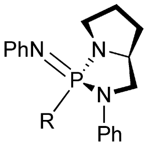
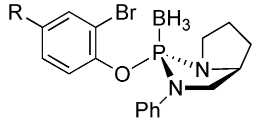
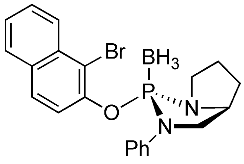
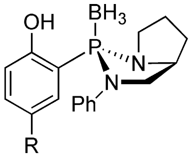
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 R = Cy, 1-Ad	B2	78–92	o.p.	Synthetic purposes	[90]
	B2/B4	–	73	Synthetic purposes	[90]
	B2/B4	–	73	Synthetic purposes	[90]
 R = Cy, ^{t}Bu, 1-Ad	A1/A3	21–32 (S_P) 12–39 (R_P)	o.p.	Synthetic purposes	[91]
 R = H, Me, CH$_2$OCH$_3$	A1	73–88 (comb.) 36–47 (purif.)	≈0 (crude) o.p. (purif.)	Synthetic purposes	[181]
 n = 0,1 R^1, R^2 = ^{t}Bu, Ph, *o*-An, 1-naphth R^3 = Me, Ph	B3	80–96 (BH$_3$) 26–82 (free)	o.p.	Pd-allylic substitution	[182]
 R^1 = Ph, 1-naphth R^2 = H, Ph	B3	47–51	o.p.	Pd-allylic substitution	[182]

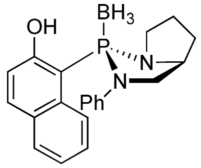
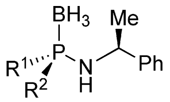
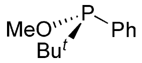
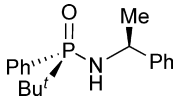
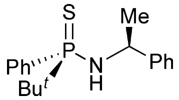
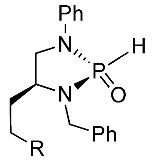
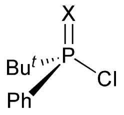
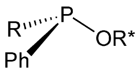
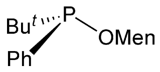
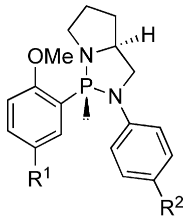
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 R = ^{t}Bu, Cy, Ph	A1/A3	62–74 (comb.)	o.p.	Synthetic purposes	[161]
 Ar = 1-naphthyl	A1	17	o.p.	Synthetic purposes	[34]
	B4	54–68	o.p.	Synthetic purposes	[223]
	B4	82	o.p.	Synthetic purposes	[223]
	B4	–	o.p.	Synthetic purposes	[223]
	A1/B2	77 (comb.)	80	Synthetic purposes	[164]
 R = Me, 2-naphth, (*S*/*R*)-Binol, 1-cyclohexene	D	75 quant.	o.p.	Synthetic purposes	[188,247]
 Ar = Ph, 2-naphth	D	quant.	o.p.	Synthetic purposes	[188,247]
	D	50	78	Synthetic purposes	[188,247]

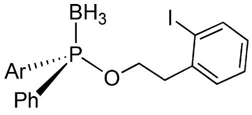
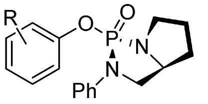
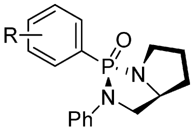
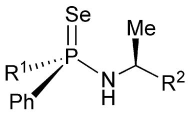
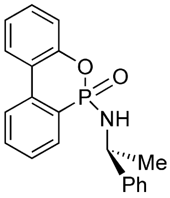
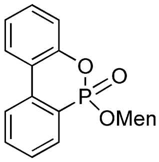
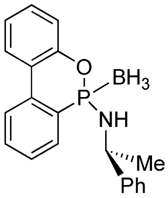
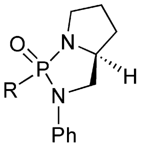
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 Ar = Ph, 1-naphth, 6-bromo-2-py	D	85–98	96–97	Synthetic purposes	[188,247]
	D	90	94	Synthetic purposes	[188,247]
	D	91	89	Synthetic purposes	[188,247]
	D	–	o.p.	Rh-hydrogenation	[192,248]
	B3	63	o.p.	Ir-hydrogenation	[193]
	A1	99	96	Synthetic purposes	[249,250]
	A1	99	94	Synthetic purposes	[249,250]
	A1	90	94	Synthetic purposes	[249,250]
	B4/D	93	o.p.	Synthetic purposes	[251]
 R = OBu, SPh, PPh_2, $P(O)Ph_2$, $P(O)(OEt)_2$, $Si(OEt)_3$, $SnBu_3$, $CH_2P(O)Ph_2$	B4/D	27–89	o.p.	Synthetic purposes	[251]

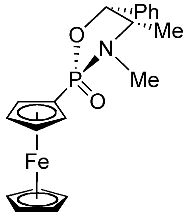
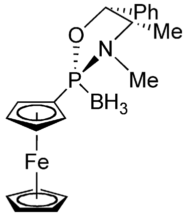
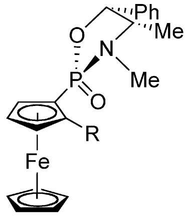
Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B4/D	53	o.p. (at P atom)	Synthetic purposes	[251]
	B4/D	89	o.p. (at P atom)	Synthetic purposes	[251]
	B4/D	78	o.p. (at P atom)	Synthetic purposes	[251]
	B4/D	43	o.p. (at P atom)	Synthetic purposes	[251]
	B4/D	97	o.p. (at P atom)	Synthetic purposes	[251]
 R = cyclopentyl, Cy	B4/D	83	o.p.	Synthetic purposes	[251]
	B4/D	45	o.p.	Synthetic purposes	[251]
	A1/D	82.5	o.p.	Synthetic purposes	[172]
 Ar = Ph, 3-py, *o*-Tol, *o*,*o*′-xylyl, 2-biph, 3-SiEt$_3$-2-biph	B1	55–87	80-o.p.	Synthetic purposes	[252]
 Ar = Ph, 2-BrPh	B1	69–78	o.p.	Synthetic purposes	[252]

Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B1	0–93	o.p.	Synthetic purposes	[252]
	B1	75	o.p.	Synthetic purposes	[252]
	B1	73	o.p.	Synthetic purposes	[252]
	B1	82	o.p.	Synthetic purposes	[252]
	B1	88	o.p.	Synthetic purposes	[252]
	B1	20	o.p.	Synthetic purposes	[252]
 X = O, S, NPh	B1	61 (free) 85 (X = O) 95 (X = S) 100 (X = NPh)	o.p.	Synthetic purposes	[253]
 R^1 = H, Me, ^{t}Bu R^2 = H, Me, ^{t}Bu, Ph, Cl	B1	58–86	o.p.	Synthetic purposes	[254]

Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 R^1 = H, Me R^2 = H, Me, Ph, Cl	B1	71–86	o.p.	Synthetic purposes	[254]
	B1	72–98	o.p.	Cu-Diels–Alder Pd-allylic substitution	[255–257]
	B1	–	o.p.	Pd-allylic substitution	[257]
	B1	–	o.p.	Pd-allylic substitution	[257]
 R = NMe_2, Ph	B1	48–61	o.p.	Cu-cyclopropanation	[258]
 R = H, Me, ^{t}Bu, Ph, F, Cl, OMe	B1	85–95 (free) 85–90 (BH_3)	o.p.	Synthetic purposes	[259]
	B1	60 (free) 70 (BH_3)	o.p.	Synthetic purposes	[259]
 R = H, Me, ^{t}Bu, Ph, F, Cl, OMe	B1	76–86	o.p.	Synthetic purposes	[259]

Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B1	40	o.p.	Synthetic purposes	[259]
 R^1 = ^{t}Bu, Ph R^2 = ^{i}Bu, Ph, Mesityl	B1	–	40–80 (free, crude) o.p. (purif.)	Synthetic purposes	[155]
	B1	80	o.p.	Synthetic purposes	[155]
	B1	80	o.p.	Synthetic purposes	[155]
	B1	50	o.p.	Synthetic purposes	[155]
 R = NHPh, NMePh, NAcPh, Ph	B1	35–80	o.p.	Pd-allylic substitution	[260,261]
 X = O, S	A1	–	50–70 (oxide) 28 (sulfide)	Synthetic purposes	[176]
 R = ^{i}Pr, ^{i}Bu, Bn	A1	70	0-o.p.	Synthetic purposes	[262]
	A1	68–73 (crude)	90 (crude) o.p. (purif.)	Pd-hydrovinylation	[263]
 R^1 = H, TBSO R^2 = Br, OMe	B1	46–63	o.p.	Pd-allylic substitution	[264]

Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
 Ar = 1-naphth	B1	24	o.p.	Synthetic purposes	[179]
	D	63–84	90–100	Synthetic purposes	[265]
	D	72–92	o.p.	Synthetic purposes	[265]
 R^1 = ^{i}Pr, Cy, ^{t}Bu, *o*-An, *p*-An, *p*-Cl-Ph R^2 = Cy, Ph, 1-naphthyl	A1	72-quant. (comb.)	0–30 (combined) o.p. (sept.)	Synthetic purposes	[266]
	A1	59 (comb.) 16 (sept.)	93	Synthetic purposes	[267]
	A1	91 (comb.) 18 (S_P) 15 (R_P)	71 (R_P) 78 (S_P)	Synthetic purposes	[267]
	A1	95 (BH_3, comb.) 38 (BH_3, sept.) 90 (free)	78 (BH_3) 78 (free)	Synthetic purposes	[267]
 R = amine, alkoxide, Cl	B1	Various	o.p. (most cases)	BH_3-reduction of prochiral ketones	[268–272]

Structure	Method	Yield (%)	e.e. or d.e. (%)	Application	References
	B1	60	o.p.	Synthetic purposes	[273]
	B1	64	o.p.	Synthetic purposes	[273]
 R = Me, I, TMS, TES, PhCOH, $B(OH)_2$, PPh_2, PCy_2, $P(p\text{-}CF_3Ph)_2$, $P(p\text{-}OMePh)_2$	B1	45–95	o.p.	Synthetic purposes	[273]

comb.: combined yield. diast. pure: diastereomerically pure. o.p.: optically pure. purif.: purified. quant.: quantitative yield. recr.: recrystallized. sept.: separated. Ad: adamantly. An: anisyl. Bor: bornyl. biph: biphenylyl. Bn: benzyl. Cy: cyclohexyl. Fc: ferrocenyl. Men: menthyl. Mes: mesityl. Ms: mesyl. naphth: naphthyl. phen: phenanthrhyl. py: pyridyl. TBSO: *tert*-butylsiloxane. TES: triethylsilyl. TMS: trimethylsilyl. Tol: tolyl. Ts: tosyl.

7. Conclusion

This review has summarized the main available methods for the synthesis of *P*-stereogenic phosphines, focusing on the most recent advances in asymmetric synthesis and catalysis. The renewed interest in this field has led to promising advances in their synthesis, although an overall methodology is still lacking, in particular for preparing very bulky phosphine ligands. At present, we are likely to see further progress in all areas, and especially in catalytic asymmetric synthesis.

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