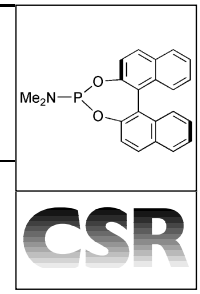
Enantioselective catalysis using phosphorus-donor ligands containing two or three P–N or P–O bonds



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This review describes some recent developments in the area of asymmetric catalysis using organometallic complexes of ligands which contain two or three P–O or P–N bonds. This category of ligands has, until the last five years or so, been underrepresented in asymmetric catalysis, particularly in contrast to phosphine ligands. Recent breakthroughs in methodology for the synthesis and manipulation of such materials have resulted in the delivery of ligands which demonstrate remarkably high enantioinduction properties in a series of asymmetric transformations.

Introduction

The use of organometallic complexes for the enantioselective homogeneous catalysis of organic reactions has been a rich area of research over recent decades, culminating in the recent award of Nobel prizes to three of the leading pioneers of the field. An industrious and sustained series of international research programmes have now delivered a number of practical catalyst systems of value to the synthetic organic chemist. Despite this impressive progress many challenges, notably with regard to extension of substrate scope, selectivity and activity, still attract the attention of the innovative catalyst designers and builders.

In the arena of homochiral organometallic catalysts containing phosphorus-based ligands, the vast majority of research has focussed on the development of *phosphine* ligands. This class of ligand notably benefits from a useful combination of well-defined structure, stability, simplicity of preparation and a capacity to induce high rate accelerations into the target reactions. In contrast, other classes of phosphorus-donor ligands such as phosphites and phosphoramidites have received a lower level of attention. The reasons for this are not immediately apparent, since phosphorus ligands containing P–O and P–N bonds may be constructed in large quantities through the use of relatively simple condensation processes, and from inexpensive starting materials. In certain cases, compounds containing P–N/O bonds have proved to be somewhat unstable, notably to protic solvents, which clearly limits their utility.

Within the last decade, however, this situation has changed. Several new classes of P–O and P–N bond-containing phosphorus ligands of high stability have been demonstrated to be capable of the acceleration and asymmetric catalysis of a number of pivotal synthetic organic reactions. These new materials have served to transform this area of research into one of intensive international activity. This review, whilst not comprehensive due to the necessity of space limitations, is intended to serve as a summary of some of the most significant recent developments in this field. It also represents an introduction to the area for those who may wish to learn more in particular about homochiral ligands containing two or three P–N and P–O bonds.†

† A large number of excellent ligands have been prepared and used which contain dialkyl or diaryl phosphine units attached to chiral backbones through P–O and/or P–N linkages. These will not be covered in this review for simple reasons of practicality and space limitations, and to allow the review to focus on other, more specialised, ligands.

Mr Jeffrey Ansell graduated from the University of Hertfordshire in 2000 with a BSc (Hons) degree in medicinal chemistry. His BSc research project under the supervision of Dr Fyaz M. D. Ismail involved the synthesis, characterisation and quantitative structure–activity relationship studies of novel 4-aminoquinoline antimalarial agents with marked activity in vivo. *He is currently studying for a PhD degree in organic chemistry under the supervision of Professor Martin Wills at the University of Warwick, where his research interests include the synthesis of novel asymmetric diazaphospholidine ligands and the application of their transition metal complexes to the enantioselective homogeneous catalysis of a variety of organic reactions.*

Professor Martin Wills was born in Swansea, Wales, in 1964, and grew up in Swansea, Cardiff and Reading. He completed a BSc at Imperial College, London in 1985 and a DPhil at Oxford University under the supervision of S. G. Davies in 1988. Following a year of postdoctoral research with the late W. Oppolzer at Geneva he was appointed to a lectureship in organic chemistry at Bath University. In 1995 he moved to a readership at Warwick University, where he is currently working on the development of novel asymmetric catalysts and synthetic methodology. In August 2000 he was promoted to a personal chair.

Ligand classification

The ligands described in this review (a total of seven P–O/N combinations can be envisaged; Fig. 1) can be conveniently

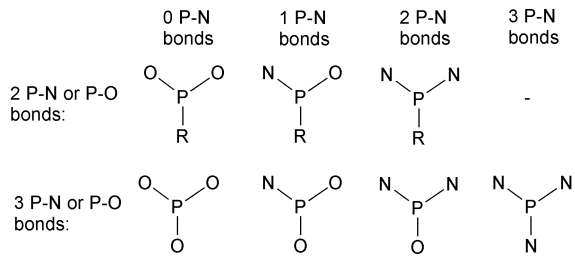


Fig. 1 Ligand classification by P–N/N–O bond.

classified in two ways, firstly; (a) containing 2 P–N or P–O bonds (three permutations) or (b) containing 3 P–O or P–N bonds (four permutations) and then again into three categories of ligands (Fig. 2) which are either; (i) 'monodonor', *i.e.* relying

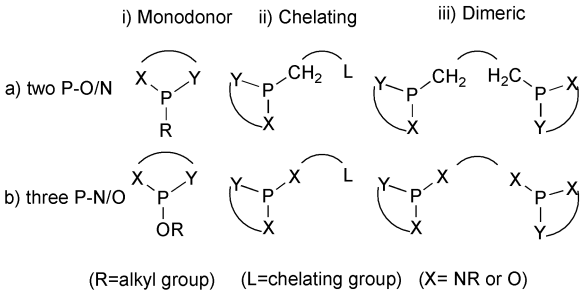


Fig. 2 Ligand classification by structure.

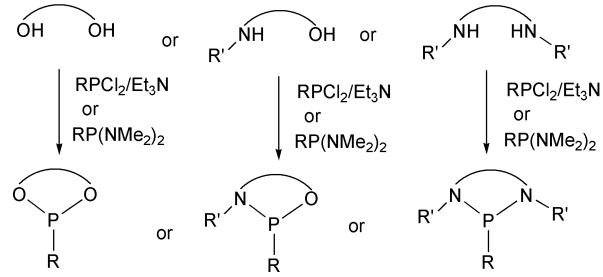
solely on the chiral environment around the phosphorus atom, (ii) 'chelating', *i.e.* containing a second donor group at a suitably close location which serves to assist the 'definition' of the chiral environment around the metal, and (iii) 'dimeric', *i.e.* containing two identical donor groups with P–N/O donor ligands.

This review will be conveniently structured to introduce the methods for the preparation and various applications of ligands in the order (a) (i)–(iii) and (b) (i)–(iii).

Ligand preparation

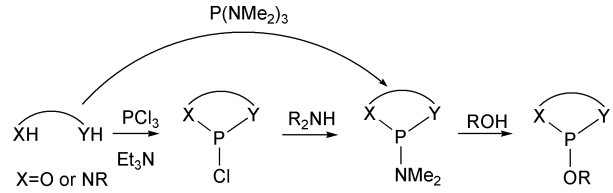
In practice, whilst not exclusively the case, the vast majority of practical homochiral ligands which contain 2 or 3 P–N/O bonds actually contain a cyclic structure in which the phosphorus atom is a component of a heterocyclic ring. Not only is this feature responsible for a dramatic increase in ligand stability relative to acyclic systems, but also sharply simplifies the preparation of the materials as well. In fact almost all the synthetic routes to these ligands involve, as the first step, the formation of the heterocycle by reaction of a diol, amino-alcohol or diamine with an appropriate P(III) compound. This process is, of course, accompanied by all the entropic advantages which cyclisation reactions provide and, for the '(a)' ligand class (2 P–N/O bonds) generally delivers the required ligands directly.

In general, the electrophilic components in the heterocycle synthesis contain either halides (usually chlorine) or dialkylamines (usually dimethylamine) as leaving groups (Scheme 1). The choice is often a question of whatever starting materials are available, however the latter class are often more practical as the only side product is a volatile gas which is often lost at the elevated temperatures of the reaction, and no base is required. In the case of chloride leaving groups, a tertiary amine base is generally required to quench the generated HCl.



Scheme 1 Synthesis of ligands containing 2 P–O/P–N bonds.

For ligands of category '(b)', *i.e.* containing three P–N/O bonds, the third group is usually introduced last. To assist this process, advantage may be taken of the general observation that, in P(III) complexes of this type, exocyclic P–O bonds are of higher stability than exocyclic P–N bonds (Scheme 2). This



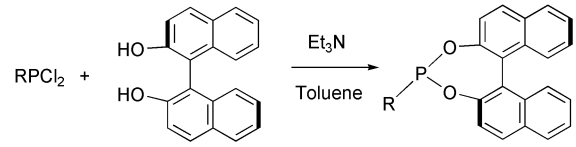
Scheme 2 Synthesis of ligands containing 3 P–O/P–N bonds.

permits a predicable series of reactions to be designed and executed towards the synthesis of any given ligand target. Any other order of reactions (*e.g.* putting in the ring as the last step) would be regarded as 'going the hard way'.

Examples of the preparation of ligands

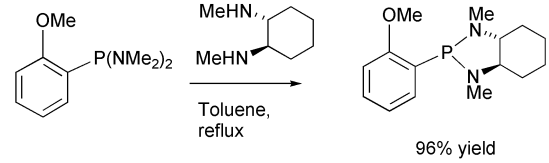
Two P–O/N, monodonor

Some of the very simplest ligands may be prepared by the reaction of phosphorus dichlorides with diols, as in the case of BINOL-derived ligands illustrated in Scheme 3.[1–3] Diamines



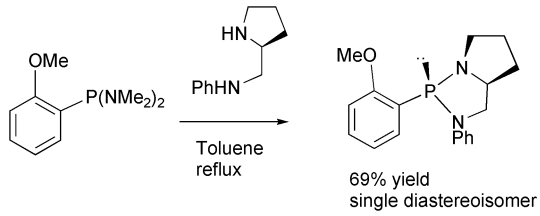
Scheme 3

may also be employed for the synthesis of diazaphospholidine monodonor ligands (Schemes 4 and 5).[4,5] In the latter two



Scheme 4

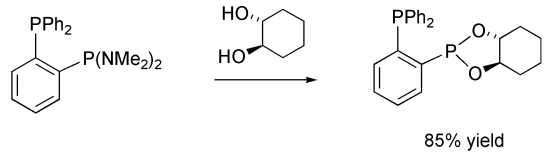
examples, the methoxy group, although potentially a chelating function, generally does not bind strongly to metals in applications, hence these ligands may be considered to be monodonor ligands. There is, however, the potential for an alkoxy group to act as a *hemilabile* ligand, and for the aromatic ring to which it is attached to bind to a metal through its π-system.



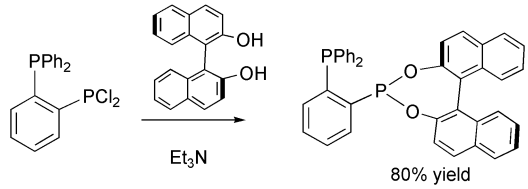
Scheme 5

Two P–O/N, chelating

Provided it is compatible with the reaction conditions, ligands of this type may be prepared by condensation reactions using electrophilic components which contain the requisite chelating group, such as a phosphine (Schemes 6 and 7).[6,7] Using this



Scheme 6

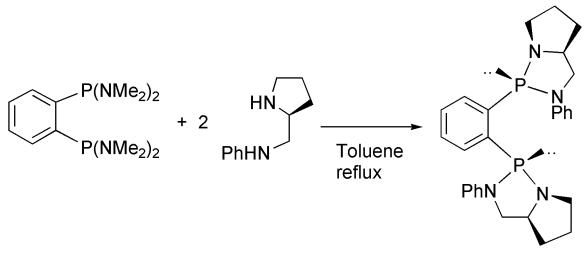


Scheme 7

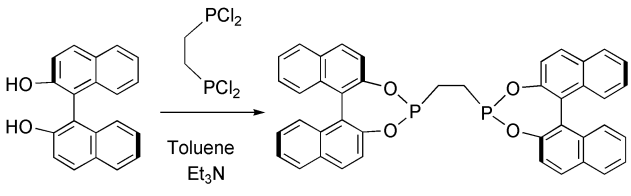
sequence, a large range of ligands can be prepared from a single common starting material, including those with chirality at phosphorus arising from the use of homochiral amino alcohols.

Two P–O/N, dimeric

Taking advantage of the symmetry of the target and, hence, the required starting materials, this class of ligand can be prepared through the use of a stoichiometrically-appropriate combination of reagents (Schemes 8[5,8,9] and 9[1–3]). It is generally difficult to introduce the heterocyclic rings one at a time.



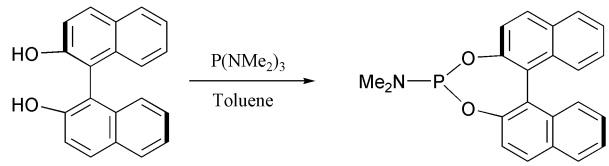
Scheme 8



Scheme 9

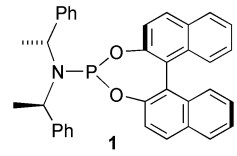
Three P–O/N monodonor

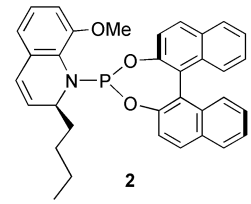
The simplest materials to prepare of this class, these are often obtained by direct reaction of a diol, amino alcohol or diamine with an appropriate P(III) compound (Scheme 10).[10] Slightly



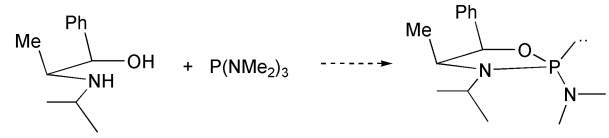
Scheme 10

more complex derivatives, such as **1** and **2**, have been prepared by prior formation of the phosphorus heterocycle containing a P–Cl bond, followed by displacement with a chiral amine.[11–14]





In the case of amino alcohol starting materials, a good degree of diastereocontrol can often be achieved, to deliver a predominant diastereoisomer of product (Scheme 11).[15–17] The

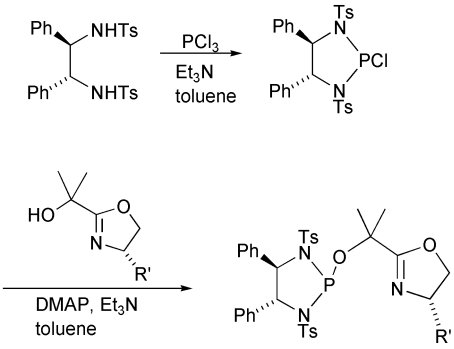


Scheme 11

chirality of the phosphorus atom in these compounds is generally configurationally rigid under the conditions for the reactions in which they are applied.

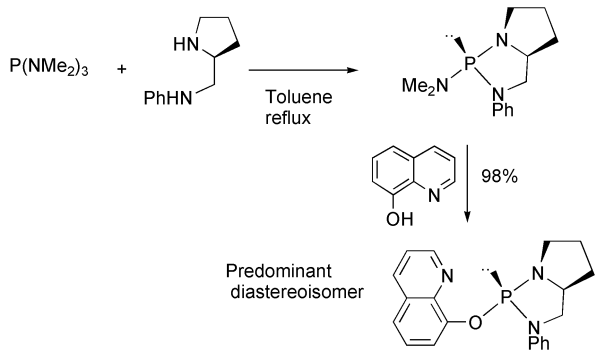
Three P–O/N, chelating and dimeric

In general the exocyclic P–O or P–N bond is best formed as the last step (Scheme 12).[18] One obvious limitation of this process



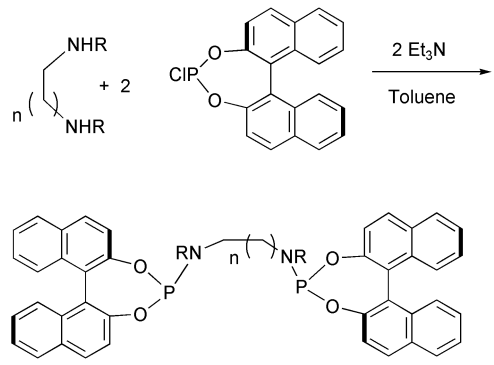
Scheme 12

is that the chelating group is required to be of a relatively inert nature, *i.e.* a heterocyclic ring or similar structure (Scheme 13).[19] If not then there is a danger that it may disrupt the structure of the original heterocyclic ring and lead to ligand decomposition.



Scheme 13

In the case of dimeric ligands, the exocyclic bonds which will form the bridge between the two components are generally introduced last, *i.e.* with the bridge going in last (Scheme 14).[20]



Scheme 14

Applications of the ligands in asymmetric catalytic applications

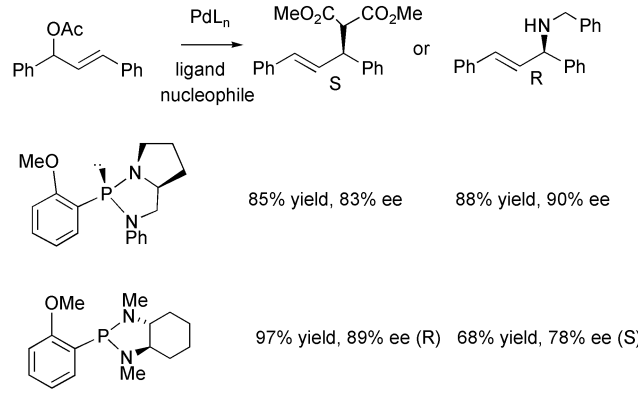
In this section of the review, there will be an emphasis on three areas of research: allylic substitution, hydrogenation and conjugate addition, as these represent the areas of the most intensive research work. A section on miscellaneous applications is also included. In each case the description of ligand applications will follow the order defined in the section on ligand preparation.

Asymmetric allylic substitution reactions

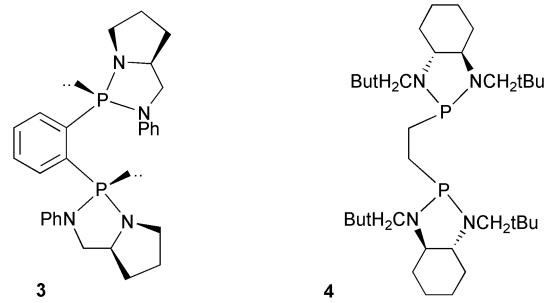
Two P–O/N, monodonor, chelating and dimeric

Relatively few ligands of this type have been used in this application. Scheme 15 illustrates two ligands which have been employed recently. Of the two ligands used, the C_1 symmetric diazaphospholidine affords the better results, probably due to a better-defined chiral environment around the P atom.[4,5]

There are no apparent examples of the use of chelating ligands for this application, however a small number of dimeric ligands have been employed, notably **3**[4,5] and **4**,[8,9] which give mixed results in terms of catalysis and enantioselectivity. Ligand **3** catalyses C–C bond formation in high e.e. but low yield, which may be a reflection of its hindered nature. Ligand **4**, with a more flexible structure, does not perform efficiently in this application.

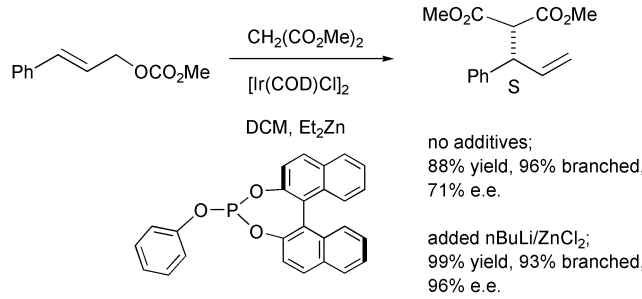


Scheme 15



Three P–O/N, monodonor

Several excellent ligands have been used in this application, notably for the control of challenging reactions with unsymmetrical allylic substrates. In many cases certain additives can have a dramatic effect on the outcome.[21] In the example illustrated in Scheme 16 a combination of lithium and zinc salts



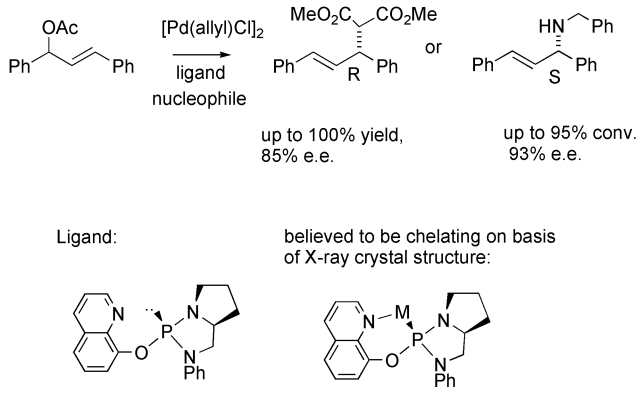
Scheme 16

affords a dramatic increase in the e.e. of the product. In another example using a closely related ligand, lithium chloride and fluoride have beneficial effects on the regioselectivity.[22]

Three P–O/N, chelating and dimeric

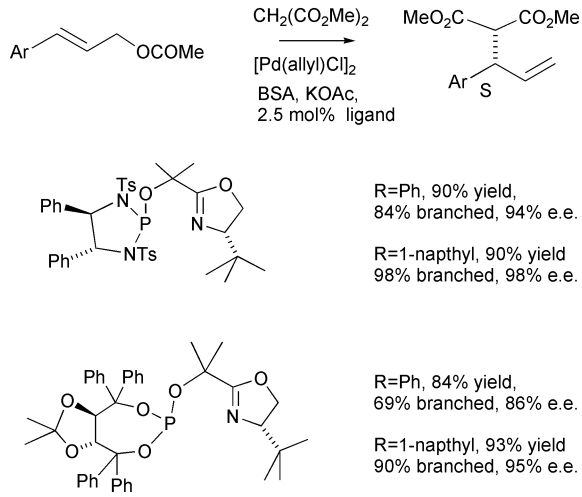
Excellent results have been achieved by Buono using an isoquinoline donor ligand in combination with a chiral phosphorus ligand unit (Scheme 17).[23–25] The chelating nature of the ligand was demonstrated by the crystal structure of a palladium derivative, in which a six-membered organometallic complex was observed. Similar ligands have been employed by other researchers, although with a combination of chiral phosphite donors with pyridine or heterocyclic units.[26]

In some comprehensive studies by Pfaltz, the use of palladium in combination with phosphite/oxazoline ligands has delivered excellent results. These ligands performed significantly better in this application than did the widely studied



Scheme 17

diarylphosphite/oxazoline donors (Scheme 18).[18,27] We were unable to identify examples of dimeric P–O/P–N bond-containing ligands in allylic substitution reactions.



Scheme 18

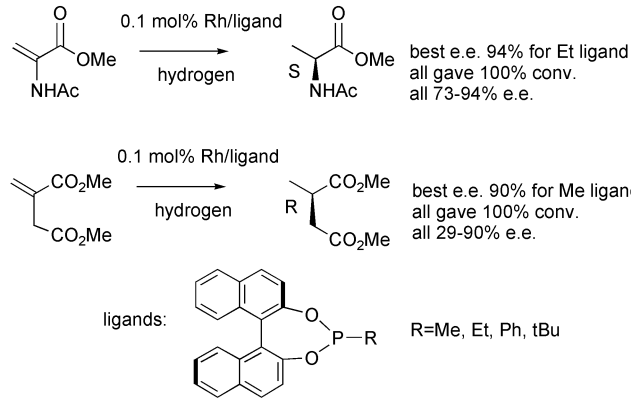
Applications of carbohydrate- and 3-hydroxypropylphosphine- derived mono/diphosphite ligands in allylic allylation of diphenyl substrates gave products with e.e.s of up to 97%. Biaryl-BINOL type diols generally give the best results, and structurally related phosphine–phosphite combinations have also been examined.[28]

Asymmetric hydrogenation reactions

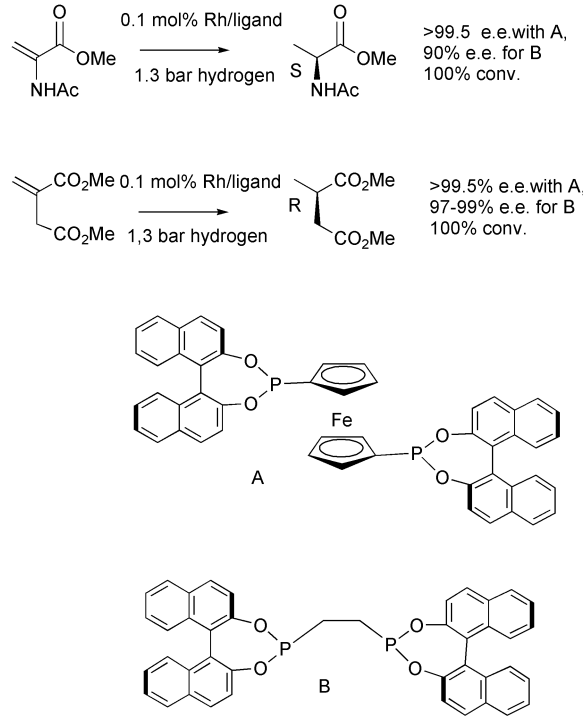
Two P–O/N, monodonor chelating and dimeric

Phosphonite ligands have emerged recently as excellent materials for the control of asymmetric hydrogenation reactions. In a series of studies which appear to have grown from earlier investigations into dimeric ligands (see a later section), monodonors have been found to outperform what might have traditionally been expected to be superior ligands (Scheme 19).[1,2] Leading exponents in this field are Reetz and Pringle, who have published very similar results independently.

No chelating ligands of this class could be found for application in asymmetric hydrogenation, however the dimeric derivatives of the monodonor ligands featured in Scheme 19 have been employed to good effect. Scheme 20 features some selected ligands based on dimeric BINOL-derived heterocycles.[2,3] It is remarkable that, whilst impressive, the observed enantiomeric excesses are comparable to the monodonor ligands illustrated in Scheme 19. This may suggest that the



Scheme 19



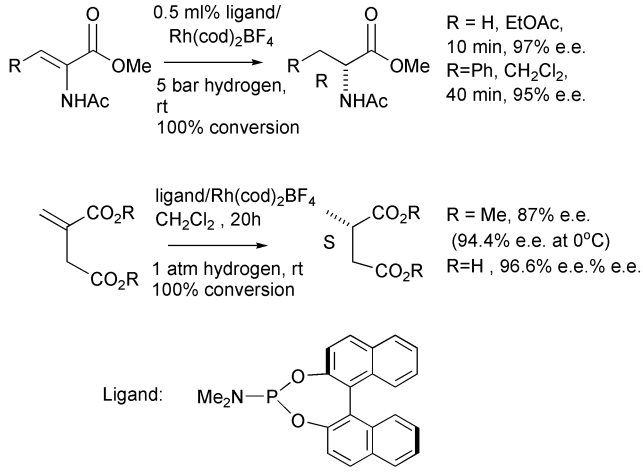
Scheme 20

BINOL unit is orientated in the same manner in complexes derived from either monodonor or dimeric ligands, thus eliminating the need for a connecting group between the two units.

Three P–O/N, monodonor

One of the most remarkable new ligands for use in asymmetric hydrogenation processes has proved to be one of the most simple. Illustrated in Scheme 21, a loading of only 0.5 mol% of a Rh complex of the phosphoramidite ligand shown is sufficient to achieve excellent hydrogenation results.[10] At slightly higher catalyst loadings the selectivities are almost perfect (99.6% e.e. at 5 mol% catalyst loading). By reducing the temperature this can be increased to 99.8% e.e. Most significantly the ligand appears to be fully stable in protic solvents, and is neither ring-opened nor decomposed under the reaction conditions.

The use of BINOL-derived structures appears to be crucial for high enantioselectivity. Closely related phosphites (dimethylamino replaced by isopropylalcohol) also perform well,[29] as



Scheme 21

do ligands containing menthol as the external group and resolving agent.[30,31] In the latter case, the BINOL stereochemistry dominates the reaction, thus diastereoisomeric ligands may be resolved and employed independently without having to perform a prior resolution of the BINOL itself.

Three P–O/N, chelating and dimeric

Ligands derived from combinations of phosphonite and phosphite (both based on BINOL scaffolds) have been employed to good effect in asymmetric hydrogenations,[32] as have phosphite/phosphine ligands[33–35] and dimeric (C_2 symmetric) diphosphites.[36] Although excellent e.e.s have been achieved, none of the results quite compare with the simplicity and elegance of the monodonor ligands, which have served to open up new avenues of interest in asymmetric hydrogenation chemistry, previously dominated by C_2 symmetric diphosphines. Use of phosphine–phosphites derived from 2-hydroxyethylphosphines and from carbohydrates have been described for the asymmetric hydrogenation of α-acylaminoacrylates: Excellent e.e.s, often up to 95%, are obtained.[37,38]

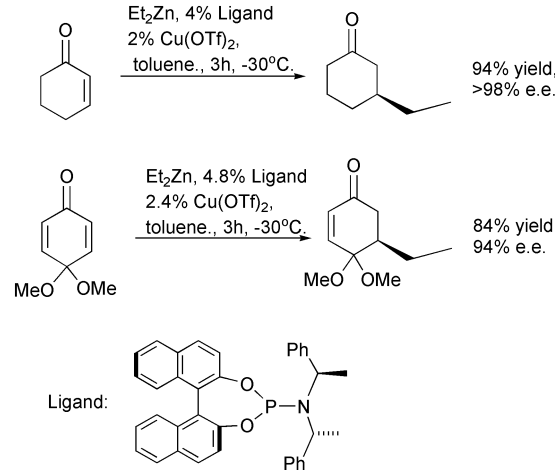
Asymmetric conjugate addition reactions

Two P–O/N, monodonor, chelating and dimeric

Although a potentially large class of ligands, few of these have been applied to the control of conjugate addition (the later sections describe more comprehensive studies). Monodonor ligands in this class derived from BINOL and related materials deliver e.e.s of up to 82% in the copper(II)triflate-promoted reaction of diethylzinc[39] with cyclohexenone (a convenient standard for comparison), although the dimeric ligands appear to be slightly superior in this case, affording up to 99% e.e. in the most recent study.[39,40] In this application the dimeric ligand derived from a ferrocene backbone has given the best set of results.[40] The optimal choice of ligand often depends upon the exact application under study; what is good for cyclohexenone may not be good for chalcone for example. This sharp contrast between ligand efficiency is illustrated in Reetz's study on the catalysis of boronic acid additions to enones (Scheme 22).[41]

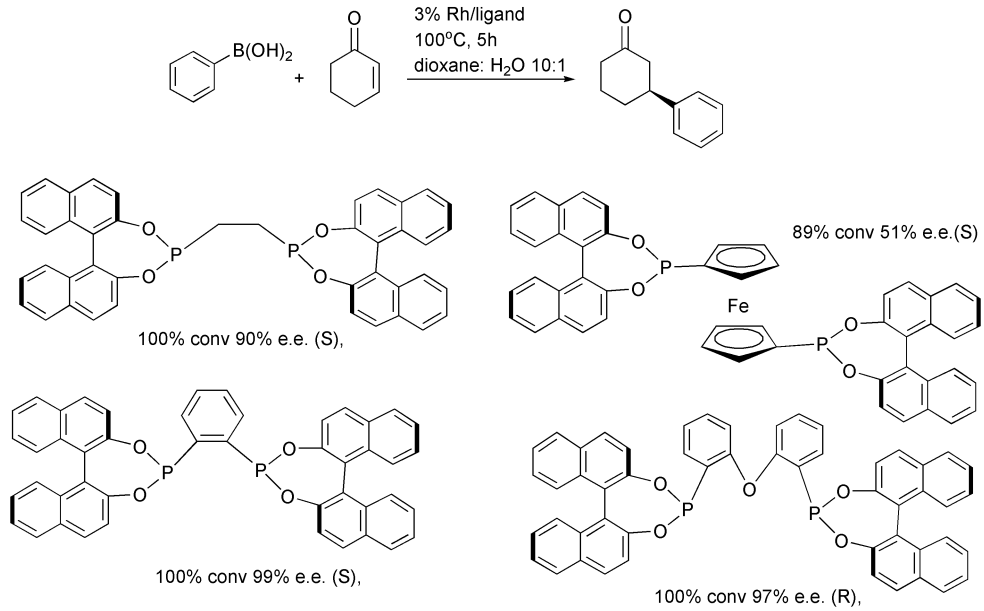
Three P–O/N, monodonor

As for the asymmetric hydrogenation work, monodonor phosphorus ligands have been demonstrated to be excellent chiral directors for asymmetric conjugate addition reactions. In particular, Feringa has introduced an excellent ligand for this application (Scheme 23), again based on the BINOL scaffold



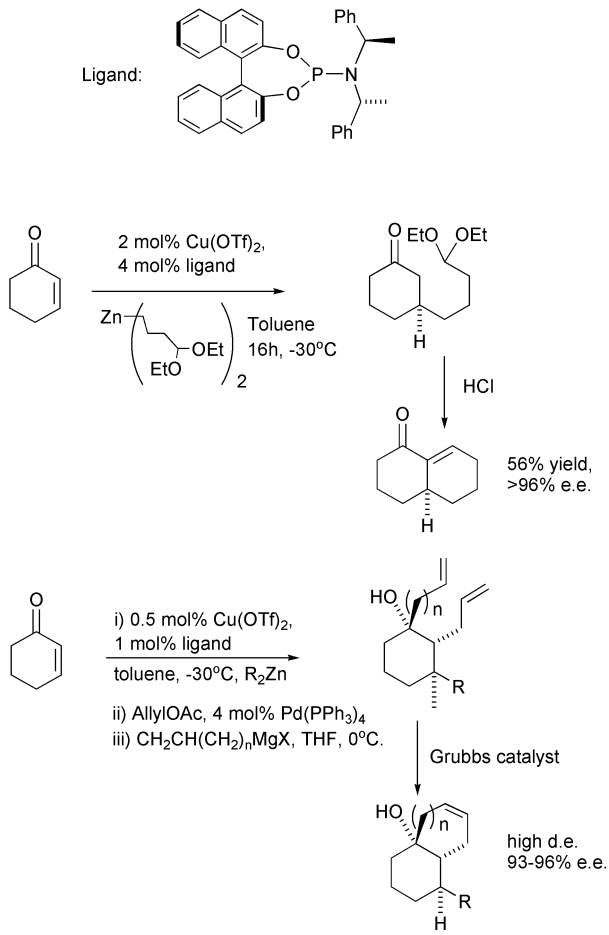
Scheme 23

and an external P–N bond. In this particular case, a slightly more complex amine was required for optimum results.[12,42–46] The conjugate trapping of the intermediate enolates delivers aldol products in excellent e.e. but moderate d.e. This ligand has since been adopted by others and employed in numerous conjugate addition applications. The mechanism has been studied in detail and non-linear effects investigated. [46]



Scheme 22

This remarkable catalyst system has been applied to the control of enantioselectivity in a number of applications, notably those in which the synthesis of a bicyclic ring structure is set up and completed; Scheme 24 features two recent examples.[11,47,48]



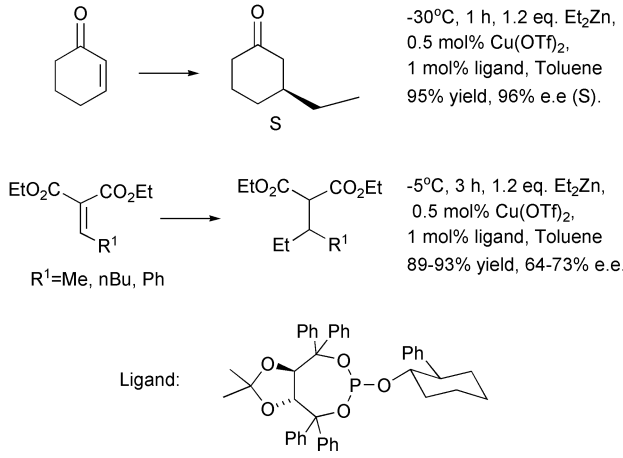
Scheme 24

The same pivotal phosphoramidite ligand has been demonstrated to be effective for the kinetic resolution of both racemic 4 and 3-substituted cyclic enones with very high selectivity.[49,50]

Several other ligands containing P–N and P–O bonds have been employed for the catalysis of conjugate addition reactions. In early work, Alexakis employed a diastereoisomerically-pure ligand derived from N–iPr norephedrine in this role for example (e.e.s up to 76% obtained).[15,16] In later work he made a key observation that, unlike other copper salts, Cu(II) triflate did not require an external ligand (phosphine, phosphite *etc.*) for its activation. However it was also noted that the used of Cu(II) triflate *together with* a phosphite resulted in the generation of a very active catalyst indeed.[51] A series of investigations into the use of homochiral phosphites derived from C_2-symmetric diols and external chiral alcohols was then undertaken. Variation of the ligand systematically and a study of the various matched/mismatched combinations has delivered TADDOL-derived phosphites as some of the very best (Scheme 25).[14,52–54] Asymmetric conjugate additions to nitroalkenes have also been described.[55,56]

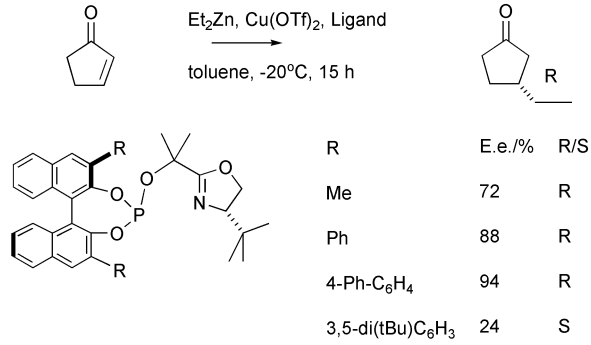
Three P–O/N, chelating and dimeric

BINOL-derived ligands containing a proximal oxazoline group have been employed for the control of the Cu(II) triflate catalysed addition of diethylzinc, and related reagents, to cyclic



Scheme 25

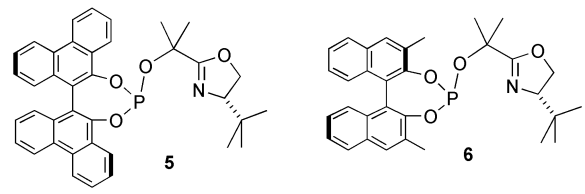
enones. A notable example is the (challenging) cyclopentenone, which forms a very reactive enolate. The fine-tuning of the ligand to this particular application requires a very precise incorporation of ligand substituents (Scheme 26).[57,58]



R	E.e./%	R/S
Me	72	R
Ph	88	R
4-Ph-C_6H_4	94	R
3,5-di(tBu)C_6H_3	24	S

Scheme 26

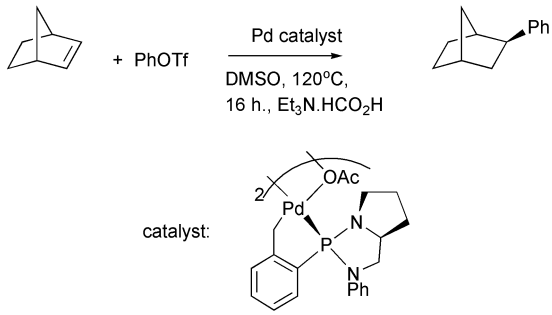
In further studies, the precise choice of BINOL derivatives has been shown to be critical for optimum results. For example ligand **5** is the best of a series for the control of diethylzinc additions to cycloheptenone, whilst **6** is the best for additions to cyclohexenone.[58] Quinoline-derived ligands have also been applied to the asymmetric catalysis of conjugate addition reactions (e.e.s up to 53%[25]), as have bidentate derivatives of the Feringa ligand **1** (up to 83% e.e.[20]) and BINOL-derived diphosphinites containing a further BINOL bridging group between the P atoms (up to 90.2% e.e. for cyclohexanone addition).[59] Glucose-derived phosphite and amino-phosphite ligands have been employed for 1,4-additions of diethylzinc giving e.e.s of up to 63%.[60]



Miscellaneous asymmetric applications

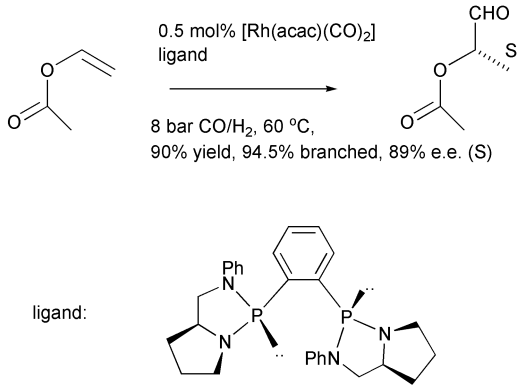
Two P–O/N, monodonor and dimeric

An unusual asymmetric Heck reaction is catalysed by the Pd-diazaphospholidine ligand (Scheme 27).[61] Although the e.e.s are low, there is promise of a great deal of potential here.



Scheme 27

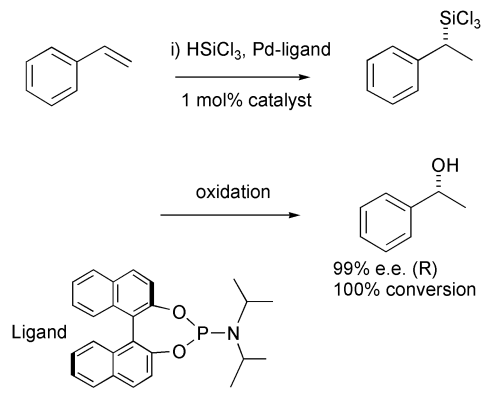
A rare example of a C_2 symmetric diazaphospholidine derivative has proved to be an outstanding ligand for the asymmetric hydroformylation of vinyl acetate. At 8 bar pressure, a product of 89% e.e. (94.5% branched) is formed (Scheme 28).[62]



Scheme 28

Three P–O/N, monodonor

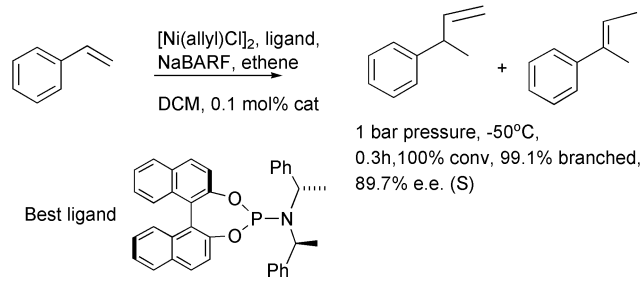
As has been previously observed when a particular class of ligand proves to be promising in one application, it is not long before its use in further reactions is examined. In what appears to be a remarkably efficient process, the bis(isopropyl) phosphoramidite ligand delivers consistently high e.e.s for a series of substrates in a remarkable hydrosilylation reaction (Scheme 29).[63]



Scheme 29

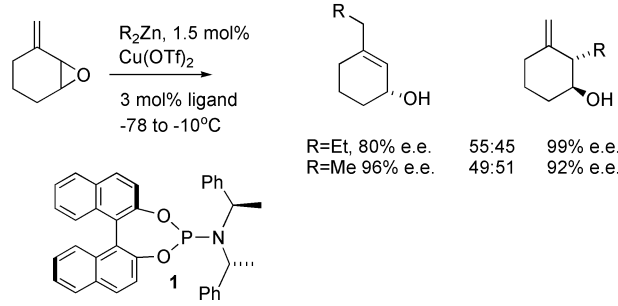
Hydrovinylation of aromatic alkenes has also been achieved in very high selectivity with the Feringa ligand **1** (Scheme 30).[13]

In recently published work,[64] the use of **1** for the control of the intramolecular Heck reaction has proved fruitful, delivering



Scheme 30

bicyclic products in very high e.e.s. The same ligand has also been applied to a series of epoxide opening reactions which serve to achieve selective parallel kinetic resolutions (Scheme 31).[65]

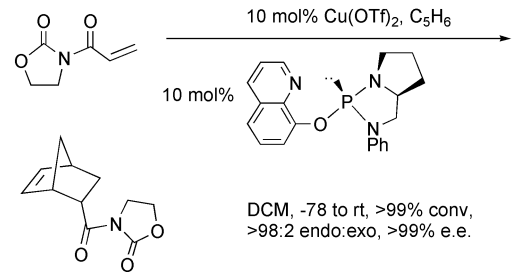


Scheme 31

Finally, in this section, the reader's attention is drawn to the early report by Pringle of asymmetric norbornene hydrocyanation by BINOL-derived phosphites (up to 38% e.e.)[66] and the use of proline-derived ligands for asymmetric catalysis of carboxylation reactions of 1-bromo-1-phenylethane by Buono (e.e.s up to 42%).[17]

Three P–O/N, chelating

An ingenious use of a quinoline-functionalised P-donor ligand has been reported by Buono for the catalysis of Diels–Alder reactions (Scheme 32).[67] Chelating ligands based on TADDOL-

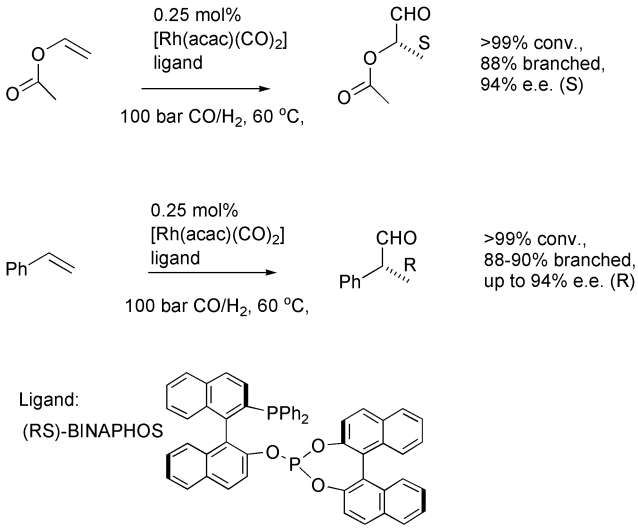


Scheme 32

derived phosphites[68] and on carbohydrate derivatives[69] have been applied to Rh(I)-catalysed hydrosilylation of ketones to good effect, giving alcohols with up to 95% e.e.

One of the most high profile phosphite/phosphine ligands to emerge in recent years has been the outstanding BINAPHOS reagent. This is an excellent ligand for hydroformylation (Scheme 33)[70,71] and propene/CO copolymerisation.[72,73]

A number of other phosphite and phosphoramidite ligands have been employed in hydroformylation reactions. Such chelating derivatives of prolinol, for example, serve to modify the platinum and rhodium-catalysed hydroformylation of sty-



Scheme 33

rene with e.e.s of up to 44%.[74] Diphosphinites derived from D-glucose give e.e.s up to 90% for aryl alkenes.[75]

Conclusions

In conclusion, it is clear that chiral phosphorus ligands containing P–O and P–N bonds have rapidly developed into valuable new materials with numerous potential synthetic applications. This has largely been the result of the development of robust and stable materials which are active and selective at very low catalyst loadings. We expect this trend to continue as further research into their applicability are investigated.

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