Part IV
Asymmetric Homogeneous Hydrogenation

The Handbook of Homogeneous Hydrogenation.
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23
Enantioselective Alkene Hydrogenation: Introduction and Historic Overview

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23.1
Introduction

This chapter describes, from an historic perspective, the development of ligands and catalysts for enantioselective hydrogenations of alkenes. There is no in-depth discussion of the many ligands available as the following chapters describe many of these, as well as their specific applications. The purpose here is to provide an overall summary and perspective of the area. By necessity, a large number of catalyst systems have not been mentioned. The discussion is also limited to the reductions of carbon–carbon unsaturation. In almost all cases, rhodium is the transition metal to catalyze this type of reduction. In order to help the reader, the year of the first publication in a journal has been included in parentheses under each structure.

Before 1968, attempts to perform enantioselective hydrogenations had either used a chiral auxiliary attached to the substrate [1] or a heterogeneous catalyst that was on a chiral support, usually derived from Nature [2]. Since the disclosure of chiral phosphine ligands to bring about enantioselective induction in a hydrogenation, many systems have been developed, as evidenced in this book. The evolution of these transition-metal catalysts has been discussed in a number of reviews [3–12].

In addition to academic curiosity, enantioselective hydrogenation catalysts have enjoyed an extra impetus for their development. The early commercial successes of Knowles with the Dopa process (*vide infra*), followed by the related applications of BINAP-based catalysts, have led many companies to develop their own ligand systems if not based on a completely new scaffold, then at least sufficiently different to allow patent protection and freedom to operate. This has resulted in a wide range of catalysts and ligand systems to perform the same, or very similar, reactions. In this chapter, ligands have been included if they have a familiar name. Acronyms are given in upper case, while the names of ligands that are not based on acronyms are given lower case with the parts of the name denoted by an upper-case letter.

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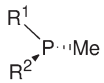
23.2
Development of CAMP and DIPAMP

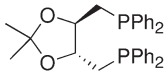
During the late 1960s, Horner et al. [13] and Knowles and Sabacky [14] independently found that a chiral monodentate tertiary phosphine, in the presence of a rhodium complex, could provide enantioselective induction for a hydrogenation, although the amount of induction was small [15–20]. The chiral phosphine ligand replaced the triphenylphosphine in a Wilkinson-type catalyst [10, 21, 22]. At about this time, it was also found that $[Rh(COD)_2]^+$ or $[Rh(NBD)_2]^+$ could be used as catalyst precursors, without the need to perform ligand exchange reactions [23].

Knowles found that the monophosphine CAMP (**1a**) could provide an ee-value of up to 88% for the reduction of dehydroamino acids. CAMP was an extension of PAMP (**1b**) that provides ee-values of 50–60% in analogous reactions [24]. At this time, Kagan showed that DIOP (**2**) (*vide infra*), where the stereogenic centers are not at phosphorus, could also provide enantioselective induction in an hydrogenation. DIOP also showed that a bisphosphine need not have the chirality at phosphorus, and that good stereoselectivity might result from a C_2-symmetric ligand. Knowles then developed the C_2-symmetric ligand DIPAMP (**3**) [22, 25]. The use of Rh-DIPAMP for the synthesis of L-Dopa is well known and is still practiced today [12, 22, 27]. A number of variations of the DIPAMP structure were investigated for the synthesis of this important pharmaceutical, but the parent remains the best ligand in this class [22].

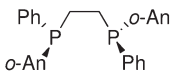


1 (1972)

a R^1 = Ph, R^2 = *o*-An (PAMP)
b R^1 = *c*-C_6H_{11}, R^2 = *o*-An (CAMP)



2 (DIOP) (1971)



3 (DIPAMP) (1977)

It is interesting to note that a few "rules of thumb" and myths came out of these early studies. Many of these have been perpetuated for decades, and the myths are only just being put to rest. Knowles showed that only two phosphorus ligands were needed on the metal to achieve reduction, and not three as in Wilkinson's catalyst [10]. The success of DIPAMP and DIOP led to the belief

that bisphosphine ligands were required for high enantioselective induction, and that C_2-symmetry was also desirable. These hypotheses molded the design of new ligands for many years. We now know that monodentate ligands, as well as asymmetric bidentate ligands, can provide high ee-values.

Another trend that arose from Knowles' results was that a wide range of enamides (dehydroamino acids) could be reduced to amino acids [22, 25, 27, 29]. This was in contrast to the enzymatic reactions known then, where enzymes were believed to be very substrate specific. As we now know, there is no general catalytic system to perform asymmetric hydrogenations and even within a small class of substrates, some ligand variation is required to achieve optimal results.

The results obtained with the Knowles' catalyst system have led to a number of useful tools that have helped with the development of other ligand families. The low ee-values obtained with simple unsaturated acids as compared to the enamides of dehydroamino acid derivatives show that the oxygen atoms of the amide is a key to complex formation with the metal center. Knowles also proposed a quadrant model that has been adapted for many reactions [5, 22]. The mechanism of the reaction has been investigated, and it is known that the addition of the substrate to the metal is regioselective and that competing catalytic cycles can occur [5, 10, 22, 25, 27, 30–46].

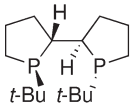
Perhaps the one major drawback with DIPAMP is the long synthetic sequence required for its preparation, though shorter and cheaper methods are now available [12]. The ligand continues to be a player for the synthesis of amino acid derivatives at scale, including L-Dopa, as mentioned above [12, 25, 27–29]. Its continued use is a testament to the power of the initial discoveries, as well as showing that a chemical catalyst can achieve selectivities only previously seen with enzymes.

The difficulty in preparing *P*-chiral ligands is a large barrier to entry for this class of ligand. It has taken over twenty years to see new, useful ligands of this class appear. BisP* (**4**) provides good selectivity for the reductions of dehydroamino acids [47, 48], enamides [49], *E*-*β*-acylaminoacrylates [50], and *α*,*β*-unsaturated-*α*-acyloxyphosphonates [51], but rates can be slow. Other ligands of this type are MiniPhos (**5**) [47, 48, 52] and the unsymmetrical **6** [53, 54], TangPhos (**7**) is also a member of the class [55–58], as are BIPNOR (**8**) [59, 60] and ^{i}Pr-BeePhos (**9**) [61]. Mention should also be made of the DuPhos-type hybrid **10** that works well for the reductions of itaconic acids [62]. A recent addition to the general class is trichickenfootphos (**11**); this has been developed for the reduction of enamides, dehydroamino acids and *α*,*β*-unsaturated nitriles [63, 64]. (Throughout this chapter, R in generic structures denotes an alkyl group unless otherwise stated.)

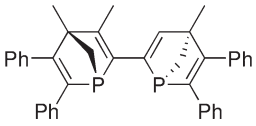
4 R = *t*-Bu (BisP*)
(1998)

5 R = *t*-Bu (MiniPhos)
(1998)

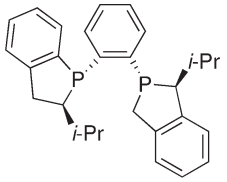
6 R =Ad, R^1 = *t*-Bu (unsymmetrical BisP*)
(2001)



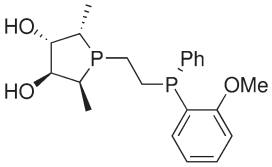
7 (TangPhos)
(2002)



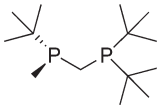
8 (BIPNOR) (1997)



9 (^{i}Pr-BeePHOS) (1997)



10 (2003)



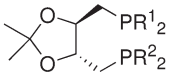
11 (Trichickenfootphos)
(2003)

23.3 DIOP

Kagan and colleagues found that DIOP (**2**) could provide significant enantioselective induction in a hydrogenation, and this finding led to Knowles' development of the DIPAMP system [65–67]. Certainly, at the time when the results were reported the ee-values were considered high, though this would not be the case today. DIOP is prepared from tartaric acid, and has the stereogenic centers in the carbon backbone rather than at the phosphorus atoms. The use of two phosphorus groups within the same molecule provided the move to the current plethora of bisphosphine ligands. The second key finding was the use of stereogenic centers in the backbone, as these are much easier to introduce than obtaining a chiral phosphorus with high enantiopurity.

DIOP has not found widespread usage after the initial investigations, presumably due to the lower selectivity.

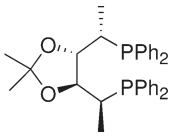
During the 1980s, Achiwa and colleagues examined a number of derivatives of DIOP, and found that MOD-DIOP (**12c**) allowed for the enantioselective hydrogenation of itaconic acid derivatives with >96% ee [68–75].



12 (1987)

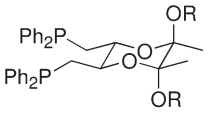
a $R^1 = R^2$ = Cy (Cy-DIOP)
b R^1 = Cy. R^2 = Ph (DIOCP)
c $R^1 = R^2$ = 3,5-Me_2-4-$MeOC_6H_2$ (MOD-DIOP)

At the turn of the millennium, Zhang and RajanBabu have independently returned to derivatives of DIOP and found that the introduction of α-methyl groups as in DIOP* (**13**) greatly increases enantioselectivity [76–79]. Zhang attributes this improvement to a reduction in the conformational flexibility of the backbone within the metal complex [3, 76]. It is interesting to note that Kagan himself prepared the *S,S,S,S*-isomer of DIOP*, but enantioselectivities were lower than with DIOP itself [80].

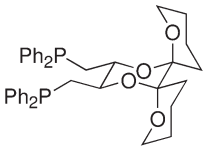


13 (DIOP*)
(2000)

The system can also be made rigid by modification of the ketal portion, as illustrated by **14** and SK-Phos (**15**). These ligands provided high stereoselection for reductions of enamides and MOM-protected β-hydroxy enamides [81].

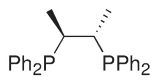


14 (2002)

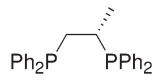


15 (SK-Phos)
(2002)

As already stated, DIOP led the way for a number of ligand systems that were built on a carbon framework containing stereogenic centers. Some of these ligands followed closely on the heels of DIOP, such as ChiraPhos (**16**) where the chelate ring is five-membered [82, 83]. Even one stereogenic center in the backbone, as in ProPhos (**17**), provides reasonable selectivity [83, 84]. The main problem with these systems is that of slow reactions.

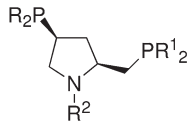


16 (ChiraPhos)
(1977)



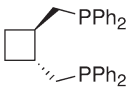
17 (ProPhos)
(1977)

Other early variations on the theme led to BPPM (**18a**) [85] and CBD (**19**) [86].



18 (1976)

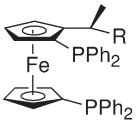
a R = R^1 = Ph, R^2 = Boc (BPPM)
b R = R^1 = Ph, R^2 = H (PPM)
c R = R^1 = Ph, R^2 = CO-*t*-Bu (PPPM)
d R = R^1 = 3,5-Me_2-4-$MeOC_6H_2$, R^2 = Boc (MOD-BPPM)
e R = Cy, R^1 = Ph, R^2 = CO_2-*t*-Bu (BCPM)
f R = Cy, R^1 = 3,5-Me_2-4-$MeOC_6H_2$, R^2 = CO_2-*t*-Bu (MOD-BCPM)
g R = Cy, R^1 = Ph, R^2 = CONHMe (MCCPM)



19 (CBD)
(1980)

BPPM is derived from 4-hydroxyproline [85]. As "unnatural" amino acids are often the target product for enantioselective reductions, Knowles' comment in his 1983 review is interesting: "BPPM, like DIOP, is a seven-membered chelator derived from natural (2*R*,4*R*)-hydroxyproline. It can give high efficiency at very fast rates. Unfortunately, it gives unwanted D-amino acids..." [22]. Although this may not be seen as a shortfall today, derivatives (**18**) of BPPM have been developed, mainly through different nitrogen substituents, and derivatives such as PPPM (**18c**) still give D-amino acids [85, 87–98]. The ligands are also useful for the reduction of itaconic acid derivatives [3].

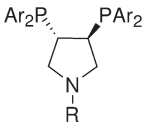
One of the branches in ligand design was provided by Kumada and his introduction of the ferrocene backbone for BPPFA [99–101] (**20a**) and BPPOH [102] (**20b**). This development leads us to the next class of ligands – ferrocene-based. Other variations for development include changes in the backbone and incorporation of the phosphorus into a phospholane (see Section 23.6).



20 (1976)

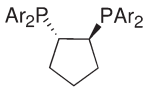
a R = NMe_2 (BPPFA)
b R = OH (BPPOH)

The electronic properties around the phosphorus atom can be varied by manipulation of the groups on that atom. MOD-DIOP (**12c**) was developed by Achiwa and used to reduce itaconic acids [68–72, 75, 103]. Some variations built on BCPM (**18e**), itself a variant of BPPM, such as the MOD-BCPM (**18f**) and MCCPM (**18g**) [88–93, 95–98, 104]. Other variants are PYRPHOS (**21a**; also called DeguPHOS) [105, 106], DPCP (**22**) [107], NorPhos (**23**) [108], BDPP (**24a**) (also called SkewPHOS) [109–111], and PPCP (**25**) [112].

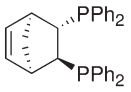


21 (1984)

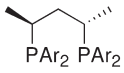
a Ar = Ph, R = CH_2Ph (PYRPHOS, DeguPHOS)
b Ar = 3,5-Me_2-4-$MeOC_6H_2$, R = CH_2Ph (MOD-DeguPHOS)



22 (DPCP)
(1983)

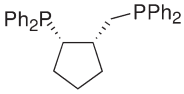


23 (NorPhos)
(1981)



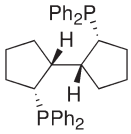
24 (1981)

a Ar = Ph (BDPP, SkewPhos)
b Ar = 3,5-Me_2-4-$MeOC_6H_2$ (MOD-BDPP)



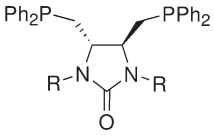
25 (PPCP)
(1991)

One ligand system which was developed during the late 1990s, and has proven quite versatile for the reduction of a wide variety of unsaturations, including *α*-and *β*-dehydroamino acids, arylenamides and MOM-protected *β*-hydroxy enamides, is the rigid BICP (**26**) [113–118].



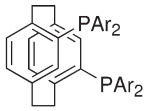
26 (BICP)
(1997)

The BDPMI (**27**) system can also be considered to be a DIOP variant, as an imidazole ring forms the rigid backbone [119–121]. Excellent stereoselectivity is seen with this system for the reductions of arylenamides.



27 (BDPMI)
(2002)

An aromatic system can also provide a rigid backbone, as seen with PhanePhos (**28a**) [122–124].



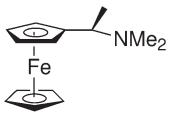
28 (1997)

a, Ar = Ph (PhanePhos)
b, Ar = 3,5-$Me_2C_6H_3$ (Xyl-PhanePhos)

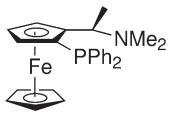
23.4 Ferrocene Ligands

Kumada's use of a ferrocene moved away from the C_2-symmetrical motive, as planar chirality can result from the two ferrocene rings having different substituents. The development of this class of ligand is well documented [5, 125–127]. The best-known uses of these ligands are for reductions of carbon–heteroatom multiple bonds, as in the synthesis of the herbicide, Metolachlor™ [128, 129].

The key access compound to the early members of the class, and indeed some later ones, is the Ugi amine (**29**) and its relationship to PPFA (**30**) and BPPFA (**20a**) can be clearly seen [100, 130, 131].

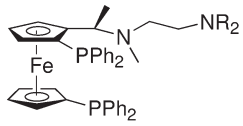


29



30 (PPFA)
(1980)

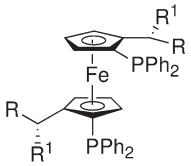
Analogues of BPPFA and BPPFOH have been prepared, but for many applications these two ligands still prove to be the best for enantioselective hydrogenations [125]. The introduction of another functional group into the side chain, as in **31**, provided the first catalysts capable of hydrogenating the tetra-substituted α,β-unsaturated acids with high enantioselectivity, even though the activity was very low (turnover frequency, TOF, $\sim 2\ h^{-1}$) [132, 133].



31 (1987)

a $R_2 = (CH_2)_4$
b R = Bu

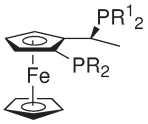
Developments after these Ugi derivatives have taken a number of pathways. The MandyPhos family of ligands (**32**) have been used to reduce enamides to *α*-amino acids as well as an enol acetate to produce an *α*-hydroxy ester [134–140]. The substituents R and R^1 can be used for the fine-tuning of a specific substrate. Many of the family have R^1 as a secondary amine, relating the family back to PPFA. For confusion, MandyPhos has also been called FerriPhos, while the derivative **32** ($R = R^1 = Et$) is known as FerroPhos.



32 (MandyPhos) (1989)
$R = R^1 = Et$ (FerroPhos)

Perhaps the first successful variation of the PPFA framework was the development of the JosiPhos family of ligands (**33**) [125, 131, 141, 142]. Here, the two phosphorus groups are attached to the same cyclopentenyl ring rather than one to each of the rings. The C_2-symmetry model is now a distant memory for these ligand families.

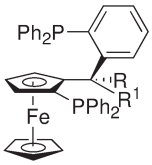
The *R,S*-family **33**, and of course its enantiomer, provide high enantioselectivities and activities for the reductions of itaconic and dehydroamino acid derivatives as well as imines [141]. The JosiPhos ligands have found industrial applications for reductions of the carbon–carbon unsaturation within *α,β*-unsaturated carbonyl substrates [125, 127, 131, 143–149]. In contrast, the *R,R*-diastereoisomer of **30** does not provide high stereoselection in enantioselective hydrogenations [125, 141].



33 (JosiPhos)
(1994)

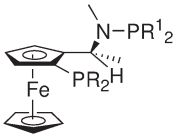
The recent introduction of the TaniaPhos ligands (**34**) provides another excellent catalyst system for the reduction of dehydroamino acid derivatives and enol

acetates [150–153]. One surprise is that the sense of induction in the product is opposite that observed with a JosiPhos-derived catalyst [125].

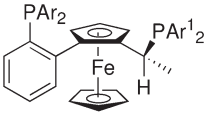


34 (TaniaPhos)
(1999)

Another ligand, the potential of which has only recently been exploited, is BoPhoz (**35**). This ligand is an aminophosphine as well as a phosphine (see also Section 23.7). It has shown high selectivities and activities with enamides and itaconates [154, 155].

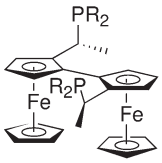


With ferrocenes, an alternative approach has been to attach the phosphorus moieties only to side chains. The WalPhos family (**36**) forms an eight-membered chelate with the metal. Members of this family provide good selectivity and reactivity for the reductions of dehydroamino and itaconic acid derivatives as well as *α,β*-unsaturated carboxylic acids [145, 156].



36 (WalPhos)
(2001)

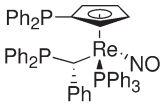
A different variation on this theme has been developed by Ito, where the TRAP ligands (**37**) form a nine-membered metallocycle [157–162]. The ruthenium catalysts seem to function best at low pressures, but highly functionalized dehydroamino esters can be reduced with high degrees of asymmetric induction [157, 159–164], as well as indoles [165].



37 (TRAP)
(1995)

where R = alkyl or aryl

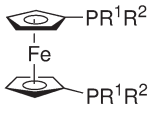
It is possible to use other metallocenes as the backbone, as illustrated by the rhenium complex (**38**) [166].



38 (2002)

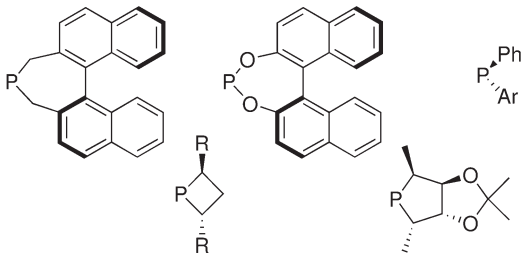
23.4.1
Ferrocene Hybrids

The rhodium complexes of the ferrocene derivatives **39** have shown useful characteristics for the reduction of itaconates as well as dehydroamino acid derivatives [15, 167–170]. These compounds are hybrids between ferrocene-based ligands and the various other types. The *P*-chiral compounds, which in some ways are DIPAMP hybrids, showed tolerance for the reduction of *N*-methyl enamides to produce *N*-methyl-*α*-amino acid derivatives [169–171].



39 (1998)

where PR^1R^2 =



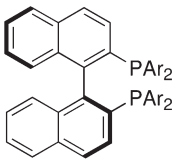
(FerroTANE)

23.5
Atropisomeric Systems

BINAP (**40a**) was first reported as a ligand in an enantioselective hydrogenation in 1980 [172], and provides good selectivity for the reductions of dehydroamino acid derivatives [173], enamides, allylic alcohols and amines, and *α,β*-unsaturated acids [4, 9, 11, 12, 174, 175]. The fame of the ligand system really came with the reduction of carbonyl groups with ruthenium as the metal [11, 176]. The Rh-BINAP systems is best known for the enantioselective isomerizations

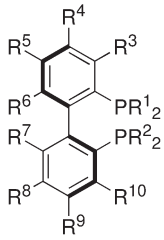
used for the industrial-scale synthesis of menthol and other terpenes [12, 177–181], rather than enantioselective hydrogenations.

The use of atropisomeric ligands for carbon–carbon bond reductions was, however, the jumping-off point for variations such as BICHEP (**41a**) [182–185], BIPHEP (**41b**) [127, 186, 187], MeO-BIPHEP (**41c**) [179, 187, 188], and Cl-MeOBIPHEP (**41d**) [189]. A slightly different approach was taken by Achiwa with the BIMOP (**41e**) [190], FUPMOP (**41 f**) [191], and MOC-BIMOP (**41g**) [192], with more substituents on the aryl rings. Again, most of the applications and high reactivities are seen for carbon–heteroatom unsaturation hydrogenations [12].



40 (1980)

a Ar = Ph (BINAP)
b Ar = *p*-MeC_6H_4 (TolBINAP)
c Ar = 3,5-$(Me)_2C_6H_3$ (XylBINAP)

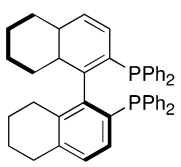


41 (1988)

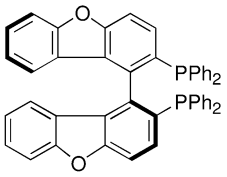
where	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	
a	Cy	Cy	H	H	H	Me	Me	H	H	H	(BICHEP)
b	Ph	Ph	H	H	H	Me	Me	H	H	H	(BIPHEP)
c	Ph	Ph	H	H	H	OMe	OMe	H	H	H	(MeO-BIPHEP)
d	Ph	Ph	H	H	Cl	OMe	OMe	Cl	H	H	(Cl-MeOBIPHEP)
e	Ph	Ph	H	Me	OMe	Me	Me	OMe	Me	H	(BIMOP)
f	Ph	Ph	H	CF_3	H	CF_3	Me	OMe	Me	H	(FUPMOP)
g	Cy	Cy	H	Me	OMe	Me	Me	OMe	Me	H	(MOC-BIMOP)
h	Ph	Ph	Ph	OMe	OMe	OMe	OMe	OMe	OMe	Ph	(*o*-Ph-HexaMeO-BIPHEP)

The success of BINAP and the associated ligands families has led to many variations, and most have shown improved properties for specific applications (Fig. 23.1). Examples include derivatives of the naphthyl system of BINAP, as well as those derived from BIPHEP.

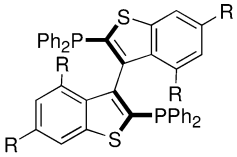
BINAP itself has been shown to be effective for the reduction of *α,β*-unsaturated carboxylic acids [8, 36, 177, 215–220], but H_8-BINAP often provides higher ee-values [193, 194]. The ruthenium complex with P-Phos provides high selectiv-



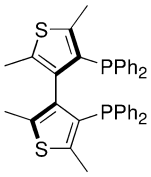
H_8-BINAP[193,194] (1991)



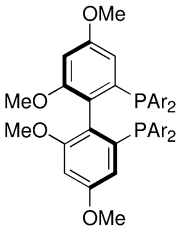
BIFAP[195] (1999)



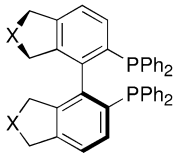
BITIANP family[196,197] (1995)
R = H, BITIANP
R = Me, TetraMe-BITIANP



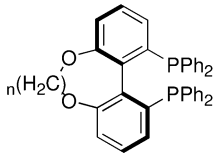
TetraMe-BITIOP
or TMBTP[198,199] (2000)



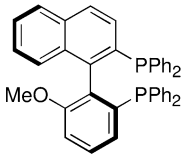
P-Phos family[200-204] (2000)
Ar = Ph (P-Phos)
Ar = *p*-MeC_6H_4 (Tol-P-Phos)
Ar = 3,5-$Me_2C_6H_3$ (Xyl-P-Phos)



X = CH_2 (SegPhos)[206] (2001)
X = CH_2CH_2 (SynPhos or
BisbenzodioxanPhos)[207,211-213]
(2002)
X = CF_2 (DiFluorPhos)[212,214]
(2004)



C_n-TunaPhos[208,209] (2000)



MeO-NAPhePhos[166,210] (2002)

Fig. 23.1 Ligands based on atropisomeric systems.

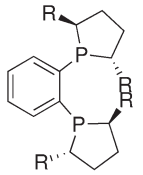
ities and reactivities with *α*-arylacrylic acids [200–202]. The rhodium complex with *o*-Ph-HexaMeO-BIPHEP works well with cyclic enamides [205].

Many of these ligands have been modified to make them water-soluble, usually by the addition of a sulfate group, or attached to a support [3, 221].

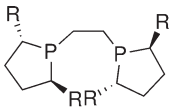
23.6 DuPhos

The development of the next major class of ligands occurred during the 1990s, with Burk's DuPhos (**42**) family of phospholane ligands [222, 223]. (An individual member of the family is named after the substituent R; in Me-DuPhos, R = Me.) This structure could be considered an improvement on the DIOP-derived ligands, where the stereogenic centers are now closer to phosphorus. In addition to the aromatic spacer of DuPhos, there is also the related BPE (**43**) family, where the spacer between the two phosphorus atoms is less rigid. In both series the phosphorus is

now part of a five-membered ring that has adjacent stereogenic centers [224, 225]. DuPhos has been shown to be useful for the preparation of α-amino acid derivatives [222, 226–241], including β-branched examples that are not accessible with DIPAMP [222, 242, 243]. The catalyst system is also successful with enamides, enol acetates, unsaturated carboxylic, and itaconic acids [7, 115, 222, 244–250].



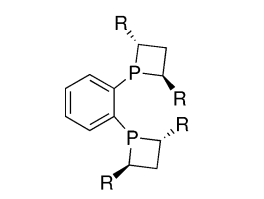
42 (DuPhos) (1990)



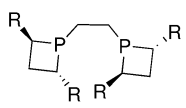
43 (BPE) (1990)

As the chirality with the DuPhos ligands is within the phospholane rings, a wide variety of backbones can be used ranging from ferrocene to heterocycles [61, 62, 77, 222, 251–262].

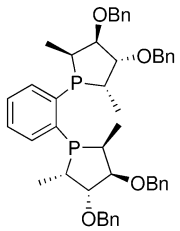
Variations have also been made on the DuPhos theme by changing the nature of the phospholane ring (Fig. 23.2). These ligands retain the high selectivity of



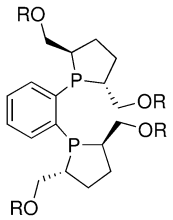
CnrPhos[168,264-268] (1997)



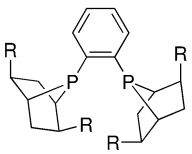
BPE-4[168,264-268] (1997)



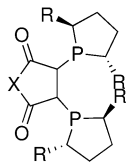
RoPhos[256,271] (1998)



BasPhos[271,272] (1999)



PennPhos[269,270] (1999)

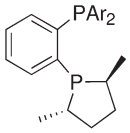


CatASium family[260] (2003)
X = O (MalPhos)
X = $(CH_2)_0$
X = NMe
X = NMeNMe

Fig. 23.2 DuPhos-derived ligands.

DuPhos. The exception for rhodium-catalyzed reductions are CnrPhos and BPE-4 [168, 264–268]. MalPhos has proven useful for the reductions of *β*-acylamino-acrylates [260]. The ferrocene hybrid (FerroTANE) was referred to earlier (see Section 23.4.1) [167, 222]. The PennPhos ligand is useful for the reductions of cyclic enamides and enol acetates; both classes of compounds are difficult for DuPhos itself to reduce with high selectivity [269, 270].

Neither of the phosphorus atoms needs not be in an asymmetric phospholane ring, as illustrated by both Saito and Pringle with UCAPs (**44**) [273, 274].



44 (UCAPs)

23.7 Variations at Phosphorus

In addition to the use of a phosphine ligands, other types of phosphorus moieties have also been used. In some cases, carbohydrates have formed the basis of the backbone, as illustrated by CarboPhos [275–280]. Some of these ligands have been available for almost twenty years. The electronic effects of the ligands can be very important with this class of compound. Other ligands of this class are variations on backbones established for bisphosphane ligands (Fig. 23.3). Most of these ligands have been employed for the reductions of dehydroamino acids; for example, the Phenyl-*β*-Glup ligand has been employed in a process involving L-Dopa [275–277].

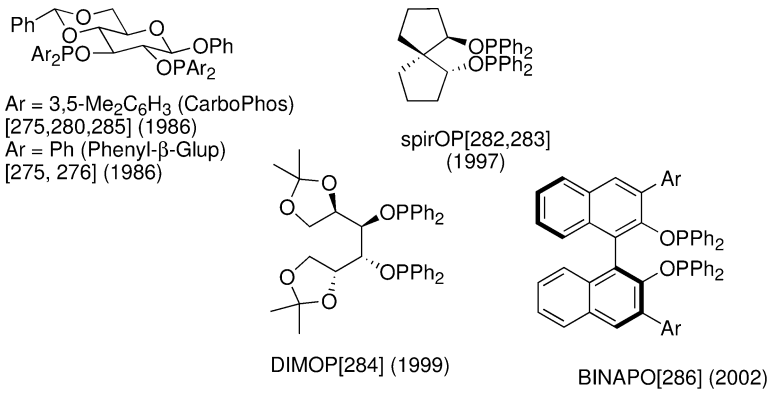
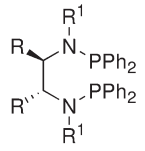


Fig. 23.3 Bisphosphites as ligands.

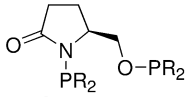
In addition to oxygen, the phosphorus can be tied to the backbone through nitrogen. Indeed, this was one of the earliest variations of the DIOP family (see Section 23.3) with PNNP (**45**) [22, 280, 287]. Care must be taken to avoid hydrolysis of the labile P–N bonds [22, 288]. Other examples of nitrogen-linked compounds are BDPAB (**46** and **47**) and its derivatives (Fig. 23.4). These ligands are clearly variations of the BINAP series [289–291].



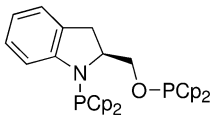
45
R = Ph, R^1 = H (PNNP)
(1979)

46 (1998)
Ar = Ph (BDPAB)
Ar = 3,5-$Me_2C_6H_3$ (Xyl-BDPAB)

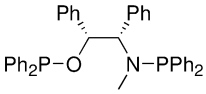
47 (H_8-BDPAB) (1998)



oxoProNOP family[293-300] (1993)
R = Cy (Cy,Cy-oxoProNOP)
R = Cp (Cp,Cp-oxoProNOP)



Cp,Cp-IndoNOP[301]
(1996)



DPAMPP[302,303]
(2000)

where Cp = cyclopentadienyl

Fig. 23.4 Ligands with phosphorus attached to the backbone through oxygen and nitrogen.

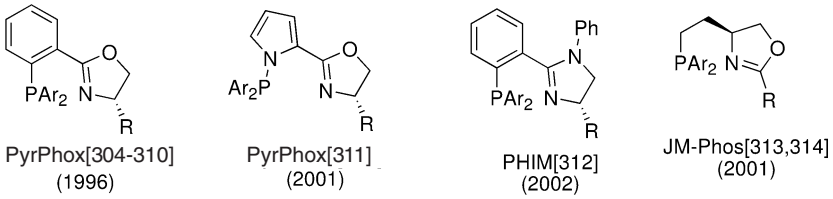
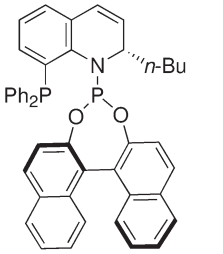


Fig. 23.5 Monophosphorus ligands.

The linkers may be nitrogen and carbon, as in BoPhoz – that is, a ferrocene-type ligand, as has already been mentioned. An example of a phosphine–phosphoramidite is provided by QuinaPhos (**48**) [292].



48 (*n*-Bu-QuinaPhos)
(2000)

In some cases, oxygen and nitrogen have been used as linkers to the backbones that are variations of those described previously (Fig. 23.4).

23.8
Monophosphorus Ligands

Just as Wilkinson's catalyst gave rise to the bisphosphine ligands, Crabtree's catalyst [304] spawned the family of phosphorus–nitrogen ligands for simple alkenes. Subsequently, Pfaltz developed the Phox family, which provides high ee-values with nonfunctionalized alkenes [305–310]. Other analogues are also illustrated in Figure 23.5.

23.9
A Return to Monodentate Ligands

The observation by Knowles that bisphosphines gave better selectivity for asymmetric hydrogenations resulted in a gap of over twenty-five years before monodentate ligands were investigated in detail and became useful ligands. There are several classes of these monodentate ligands (Fig. 23.6), all of which were introduced within a surprisingly short time period [314]. BINOL has proven to be a very successful backbone with this class of ligand, and covers phosphites (**49**),

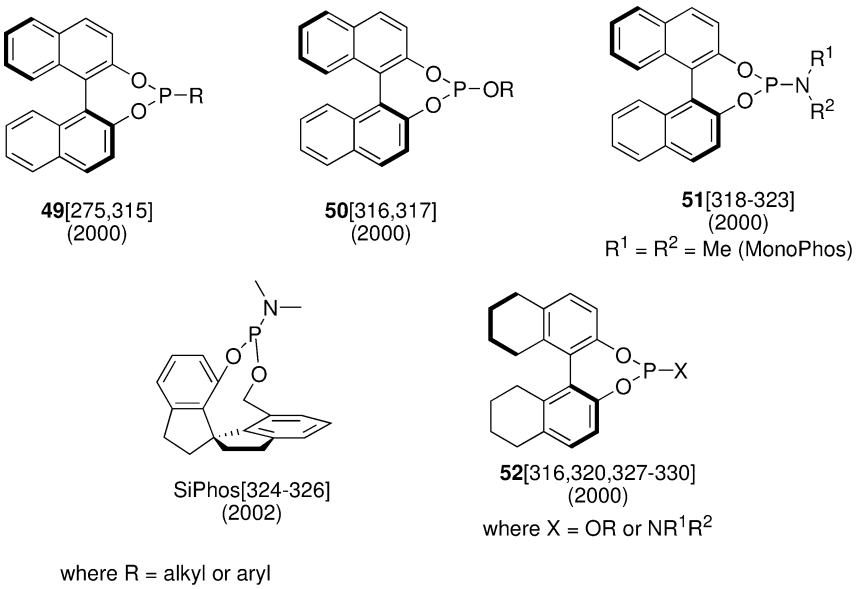


Fig. 23.6 Examples of monodentate ligands.

phosphinites (**50**), and phosphoramidites (**51**). Other variations include SiPhos, as well as reduced aromatic systems (**52**).

These ligands can be used to reduce a wide variety of carbon–carbon unsaturations, and have the advantage that their simple preparation can be used for rapid ligand library synthesis and screening [314, 318, 319, 330, 331].

23.10 Summary

The development of ligands and catalytic systems for the enantioselective hydrogenation of carbon–carbon unsaturation has been rapid, but was given an astounding start by the studies of Knowles, followed by the key findings of Kagan and colleagues. Many derivatives of these ligands have since found a place in the arsenal of the synthetic chemist. Both, Togni's ferrocene-based ligands and Burk's DuPhos family, have expanded the substrate potential of the approach as well as providing for higher selectivities and reactivities. However, recent studies have seen a return to *P*-chiral ligands, while another fairly recent contribution has come from the monodentate ligands of Pringle, Reetz, Feringa, Minnaard, and de Vries. With studies in other areas also beginning to bear fruit, it is possible that we will shortly see ligands based on alkenes making a significant impact. Although there is no "general" catalyst, there is still room for improvement with many potential substrate classes; clearly, the number of ligands appearing in the literature will continue to increase.

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