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Review

Use of sugar-based ligands in selective catalysis: Recent developments

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ABSTRACT

This review describes recent development in the use of sugar-derived ligands in the selective synthesis of organic molecules. Developments in the recent literature (2004–2009) are highlighted in the areas of hydrogenation, 1,2- and 1,4-additions of nucleophiles to C=O and C=NR based substrates, cross-coupling, hydroformylation, oxidation and other reactions. Connections to earlier studies are also noted were relevant. Some suggestions as to the underlying features that make sugar-based ligands highly useful modular ligands in selective catalysis are given. Finally, advice is presented (for the non-specialist) on optimal entry points and basic starting materials for sugar-ligand synthesis.

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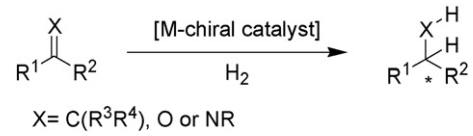
1. Introduction

This overview complements and updates developments in the area of carbohydrate-derived ligands since this was last comprehensively covered by some of us in 2003–2004 and extended in 2007 [1]. Some additional compilations of relevance have appeared in the areas of: phosphites and related ligands (including some sugar-based ligands) in 2008 [2]; and selected applications of carbohydrates in organic synthesis (including ligands and organocatalysis) in 2007 [3]. This particular review concentrates on ligands with sugar cores and focuses on underlying reasons as to why application of such species can be so successful. To begin with it is useful to briefly reiterate some key features of carbohydrate chemistry and nomenclature for the non-specialist. Acetal protection is an attractive method for improving the organic solvent solubility and handling characteristics of polyol sugars. Thermodynamic control in 5-ring acetals leads to *cis* placement of 1,2-related diols frequently delivering so called furanoside cores. Benzaldehyde derived 6-ring acetals protect the 4,6-related diols of C_6 sugars under kinetic control reinforcing the preponderance of the 6-ring pyranose forms. These relationships are summarized graphically in Fig. 1 for some of the most commonly used sugar-ligand precursors.

Anomeric effects induce the expected lability of hemiacetal OR (R = H, alkyl, aryl) groups at C-1 for aldehydic sugars, such that a mixture of α (OH down in the D series) and β (OH up in the D series) epimers can be encountered. Sugar-ligand cores are commonly retained at their aldehyde oxidation state level. However, in the case of (D)-mannose its reduction product (D)-mannitol is frequently preferred as the higher symmetry C_2-polyol frequently simplifies the subsequent synthetic routes. Although this review concentrates on sugars we have included glucosamine-derived aminosugar ligands. Sugars, and related amino sugars, constitute structurally diverse renewable resources that are available at very low cost. Methods for overcoming the natural limitations associated with having a single naturally occurring stereochemical series and robust efficient entry points to sugar-ligand cores, for the non-specialist, are dealt with specifically in Section 8.



Scheme 1. Asymmetric hydrogenation of C=C, C=O and C=N double bonds.

2. Hydrogenation

The asymmetric hydrogenation of C=C, C=O and C=N double bonds (Scheme 1) is widely used to prepare high-value compounds in several important areas such as pharmaceuticals, agrochemicals, fine chemicals and natural product chemistry [4]. For the hydrogenation of functionalized olefins and ketones, rhodium and ruthenium complexes containing phosphorous and nitrogen chiral ligands have shown to be the best catalysts. Excellent activities and enantioselectivities have been achieved along the last decades for asymmetric hydrogenation of dehydroaminoacid and other functionalized alkenes and ketones. For the hydrogenation of unfunctionalized olefins and imines, iridium complexes have became the most successful catalysts. Although significant progress has been made in this area over the last years, these asymmetric hydrogenations remain a challenge for numerous substrates.

This chapter aims to discusses the most important results and applications of metal transition catalysts containing sugar-based ligands in asymmetric hydrogenation of C=C, C=O and C=N substrates. The following sections are organized according the nature of the ligand.

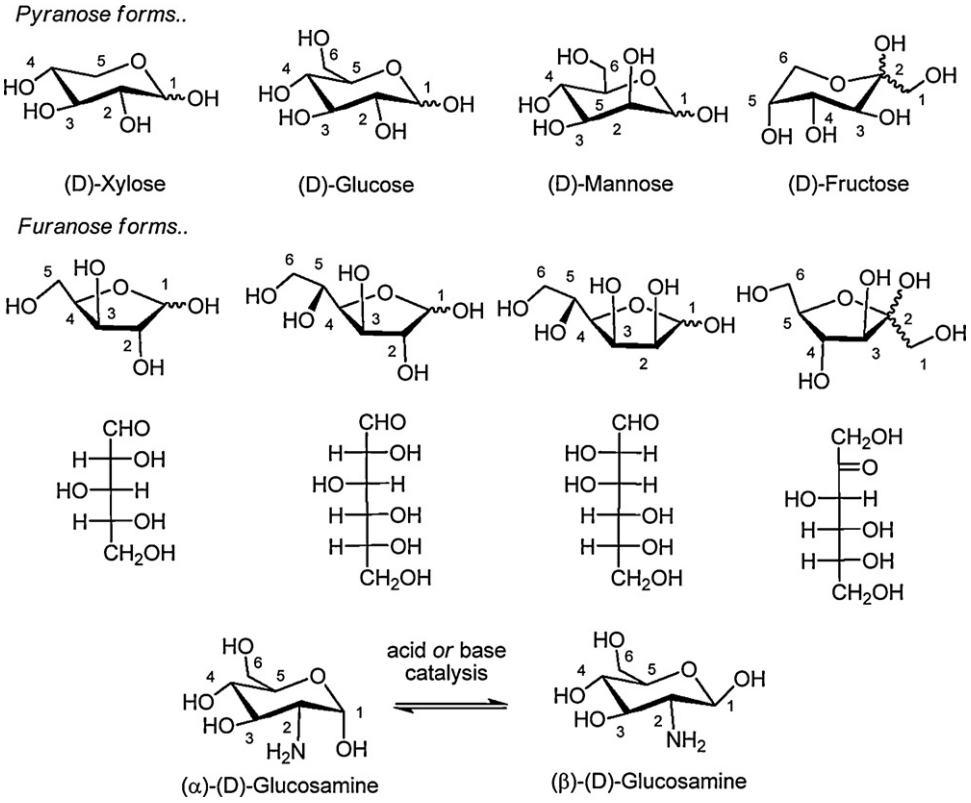


Fig. 1. Common (D)-sugar-ligand precursors and their pyrano and furano relationships to classic Fischer projections together with the pyrano form of (D)-glucosamine.

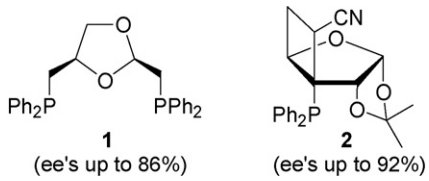


Fig. 2. Phosphine ligands **1** and **2**. In brackets, the best enantioselectivities obtained are shown as examples.

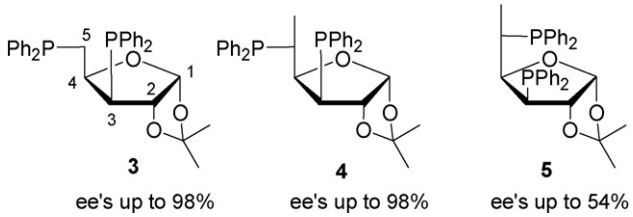


Fig. 3. Diphosphine ligands **3**–**5** with furanoside backbone derived from D-(+)-xylose and D-(+)-glucose. In brackets, the best enantioselectivities obtained are shown as examples.

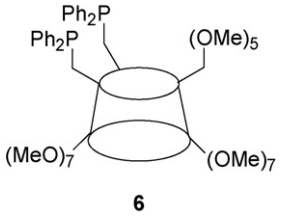


Fig. 4. Cyclodextrin-based diphosphine ligand **6**.

2.1. Homodonor ligands

In the early days, diphosphines were the most widely used phosphorous ligands providing excellent levels of enantioselectivity for asymmetric hydrogenation of functionalized C=C and C=O bonds. In this context, several phosphine carbohydrate-based ligands were developed since the early 1970s but only few of them provided high enantioselectivities. In recent years, chiral diphosphites and diphosphinites have emerged as new successful types of ligands [2]. Their highly modular construction, facile synthesis from readily available chiral alcohols, greater resistance to oxidation than phosphines and π-acceptor capacity have proved to be highly advantageous. For these reasons, several carbohydrate-based diphosphinite and diphosphite have been developed. Homodonor dithioether ligands have also been developed but with moderate success [5].

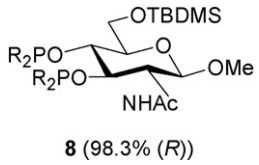


Fig. 6. 3,4-Diarylphosphinite ligands **8**. In brackets, the enantioselectivities obtained in the hydrogenation of methyl α-acetamidocinnamate are shown as examples.

2.1.1. Phosphine ligands

The first sugar-based chiral ligands used in asymmetric hydrogenation were phosphines. During the 1970s and 1980s several phosphine ligands with carbohydrate backbones were developed [6]. However, only the diphosphine ligand **1** [6c] and the monophosphine ligand **2** [6n] have shown high enantioselectivities in the reduction of dehydroaminoacid derivatives (Fig. 2).

Following these pioneering works only two new families of diphosphine ligands have appeared. The first is a series of C_1-diphosphine ligands **3**–**5** with furanoside backbone (Fig. 3). They were applied in the Rh-asymmetric hydrogenation of α,β-unsaturated carboxylic acid derivatives with better success (ee's up to 98%) [7]. The results indicated that introducing a methyl substituent at C-5 in ligand **3** significantly increased activity (TOFs were approximately double for ligands **4** and **5**). Moreover, the configuration of C-5 strongly influenced enantioselectivity. By comparing ligands **4** and **5**, therefore, we can see that the best results were obtained with ligand **4** with an *R*-configuration at C-5.

The second ligand type incorporates the phosphine functionalities into cyclodextrins (ligand **6**, Fig. 4) in order to take advantage of the properties of cyclodextrins as water soluble chiral supports [8]. Ligand **6** contains diphenylphosphine groups in two of the positions 6 of a β-cyclodextrin. The Rh/**6** catalytic system provided good enantioselectivities in the hydrogenation of α,β-unsaturated carboxylic acid derivatives (ee's up to 92%), but only organic solvents were used for these reactions.

2.1.2. Phosphinite ligands

The first examples of the use of diphosphinite ligands with carbohydrate backbone in asymmetric catalysis were reported by the groups of Cullen and Sugi [9], Jackson and Thompson [10], Selke [11] and Sinou and Descotes [12]. They studied a wide variety of 2,3-diphenylphosphinite pyranoside ligands in the asymmetric hydrogenation of dehydroamino acid derivatives. In particular, the best enantioselecitivities (ee's up to 96.6%) were obtained with a series of β-glucopyranoside 2,3-diphosphinite ligands **7** (Fig. 5, R = Ph, R′ = Ph, Me), mainly developed by Selke and coworkers [9,10,11,13] Later, RajanBabu and coworkers has studied further modifications in this ligand type **7** (R′ = Ph; Fig. 5) [14,15]. The Rh-hydrogenation results showed that electron-rich diphosphinite ligands considerably increased enantioselectivities whereas

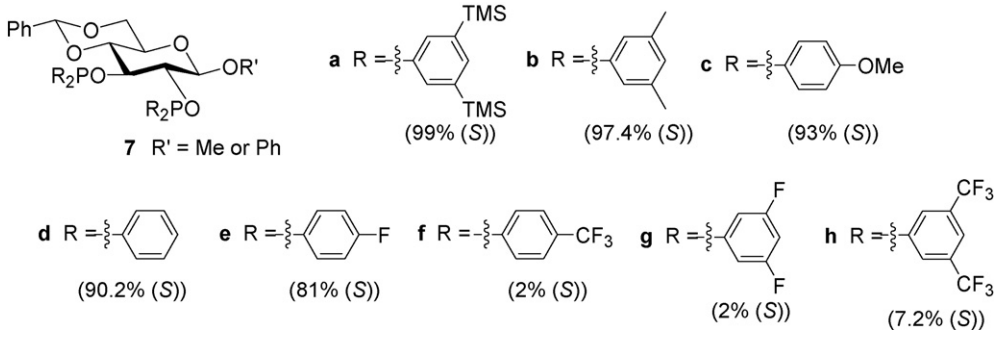


Fig. 5. Modifications of diphosphinite ligand **7**. In brackets, the enantioselectivities obtained in the hydrogenation of methyl α-acetamidocinnamate are shown as examples.

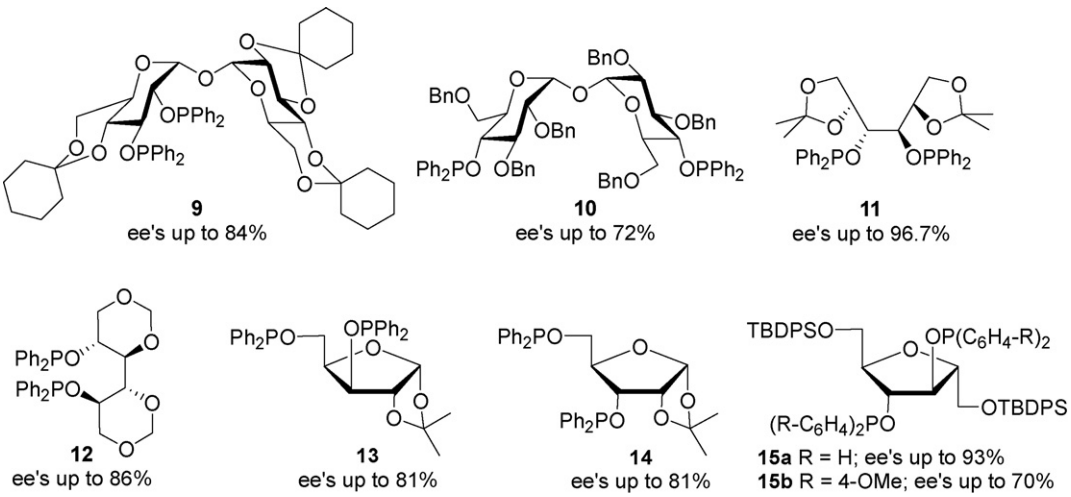


Fig. 7. Diphosphinite ligands **9**–**15**.

electron-deficient ligands provided much lower selectivity. Enantioselectivities were therefore excellent over a wide range of dehydroamino acid derivatives with ligands **7a** and **7b** (ee's up to 99% (*S*)). In all cases the *S*-enantiomer of the hydrogenation product was obtained.

In the search for the *R*-enantiomer of the hydrogenation product (D-amino acids), rather than preparing the corresponding diphosphinite **7** from the expensive L-glucose, RajanBabu and coworkers developed pseudo-enantiomeric diphosphinite ligands **8** (Fig. 6) [14]. Ligands **8** provided the highest enantioselectivities in favour to the *R*-enantiomer of the 3,4-diphosphinite series (Fig. 5). As before, enantioselectivities were best with electron-rich phosphinites (ee's up to 99% (*R*)). In summary, these sugar-diphosphinite ligand systems developed by RajanBabu appears to be among the most practical ligands for the synthesis of (*S*) and (*R*)-aromatic and heteroaromatic alanine derivatives.

After this, several new carbohydrate-based ligands were developed (Fig. 7). Uemura and coworkers developed novel disaccharide diphosphinite ligands **9** and **10** derived from α,α-trehalose (Fig. 7). These work as ligands in the Rh-catalyzed asymmetric hydrogenation of dehydroamino acid derivatives to afford both enantiomers of amino acids (ee's up to 84%) [16,17]. Later, diphosphinites **11** and **12** derived from D-mannitol have also been successfully applied in asymmetric hydrogenation (Fig. 8). Therefore, ligand **11** provided ee's up to 96.7% in the Rh-catalyzed hydrogenation of α-acetamidoacrylic acid [18] and ligand **12** gave enantioselectivities as high as 86% in the Rh-catalyzed hydrogenation of ketones, α-ketoesters and α-ketoamides [19].

In recent years, new furanoside diphosphinite ligands (**13**–**15**; Fig. 7) have been designed and successfully applied in the asymmetric hydrogenation processes [6l,20,21]. Ligands **13** and **14**, derived from D-xylose, provided ee's up 81% in the metal-catalyzed hydrogenation of several dehydroaminoacids and itaconates [20]. The results indicated that the metal source and the absolute configuration of the C-3 stereocenter of the carbohydrate backbone had an important effect. The catalytic Rh-**13** and Ir-**14** diphosphinite system therefore provide ee's up to 81%, while the other combinations provide ee's up to 15% [20]. Ligand **13** was also applied in the Ir-catalyzed asymmetric hydrogenation of imines with moderate success (ee's up to 57%) [22]. Ligand **15a** was successfully applied in the Rh-catalyzed hydrogenation of dehydroaminoacid derivatives (ee's up to 93%), whereas ligand **15b** was succesfully applied in the Ir-catalyzed hydrogenation of imines (ee's up to 70%) [21].

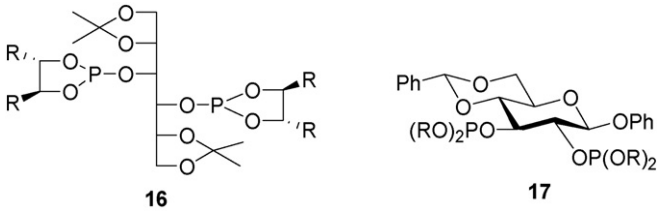


Fig. 8. Diphosphite ligands **16** and **17**.

2.1.3. Phosphite ligands

The first reports on the use of sugar-based diphosphite ligands in asymmetric hydrogenation were introduced by Brunner [6l] and Selke and coworkers [23] and led low-to-moderate enantioselectivities (Fig. 8).

An important breakthrough in the use of phosphite ligands for asymmetric hydrogenation came with the work of Reetz and coworkers. These authors developed a series of C_2-derivative ligands derived from D-mannitol **18** with different phosphite substituents (**a**–**e**) (Fig. 9) [24]. These ligands were efficiently applied in the Rh-catalyzed hydrogenation of dimethyl itaconate and methyl *N*-acetamidoacrylate. The best enantioselectivities (ee's up to 94.5%) were obtained using ligand **18e**.

These excellent results have led to the recent development of other carbohydrate phosphite ligands. In this context, a series of highly modular C_1-diphosphite ligands **19**–**24** (Fig. 10), with furanoside backbone, were developed for the Rh-catalyzed hydrogenation [1c,25]. These ligands are derived from D-(+)-xylose and D-(+)-glucose. Excellent enantioselectivities (ee's up to >99%) and activities were achieved in the Rh-catalyzed hydrogenation of several dehydroamino acid derivatives. Systematically varying stereocenters C-3 and C-5 at the ligand backbone showed that enantiomeric excesses depended strongly on the absolute configuration of C-3 and depended slightly on that of the stereocenter carbon C-5. Enantioselectivities were therefore best with ligands **21d** with *R* configuration on both C-3 and C-5 stereocenters. Ligands **19** were also applied in the Ir-catalyzed asymmetric hydrogenation of imines with moderate success (ee's up to 46%) [22]. Ru-nanoparticles stabilized with ligands **19** were used in the asymmetric hydrogenation of arenes. Although good activities and diastereoselectivities were achieved, no significant levels of enantioselectivity were obtained [26].

More recently C_2-symmetrical furanoside diphosphite ligands **25**–**28** (Fig. 11), related to the diphosphinites **15**, have been synthesized starting from D-glucosamine and D-glucitol [27]. These

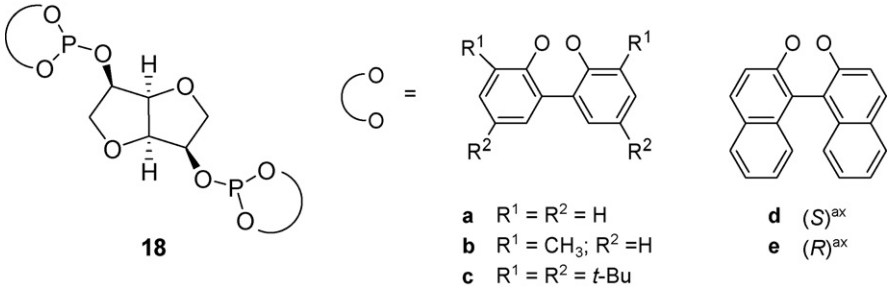


Fig. 9. D-Mannite diphosphite ligands developed by Reetz et al.

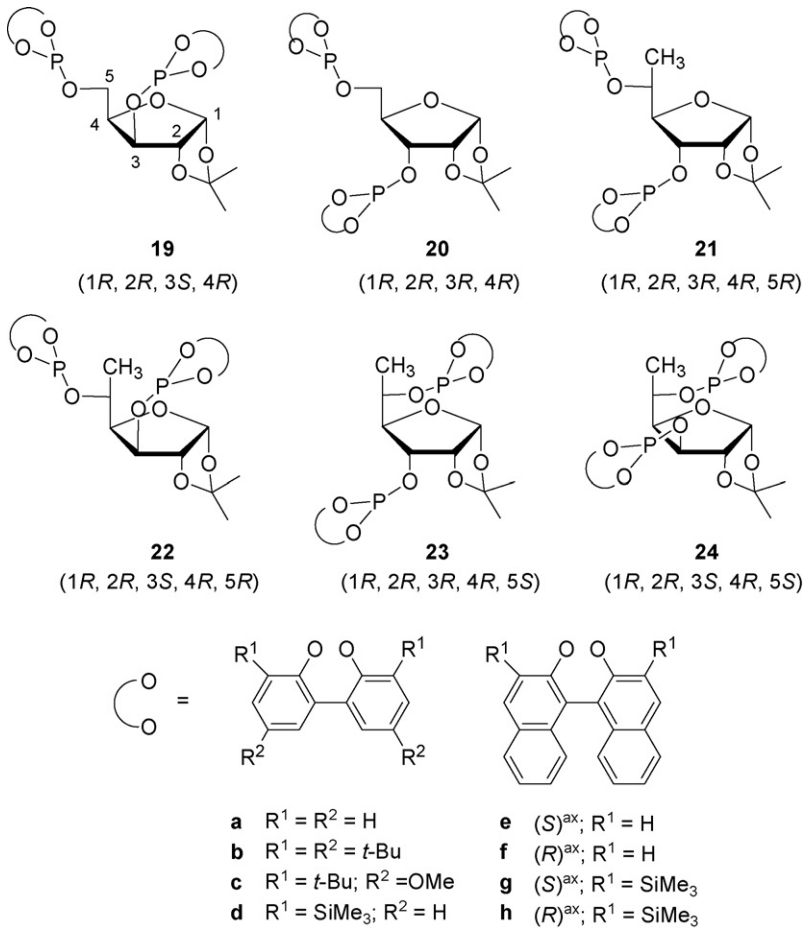


Fig. 10. Diphosphite ligands **19**–**24** with furanoside backbone.

ligands were used in the Rh-catalyzed asymmetric hydrogenation of methyl acetamidoacrylate providing much lower enantioselectivities (ee's up to 57%) than the obtained with the corresponding diphosphinites **15**.

The group of Matt and coworkers have successfully applied the diphosphite ligand **29** (Fig. 12), built on a cyclodextrin scaffold, in the Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate with ee's up to 83.6% [28].

In the last few decades it has generally been accepted that enantioselective hydrogenation was more effective in the presence of bidentate ligands. Recently, however, monophosphorus ligands have been found to be very efficient for the Rh-catalyzed asymmet-

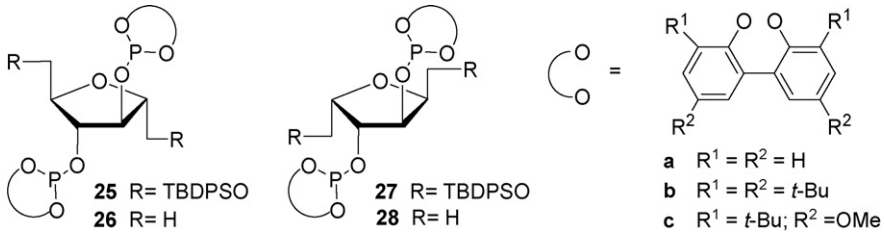


Fig. 11. Diphosphite ligands **25**–**28** with furanoside backbone.

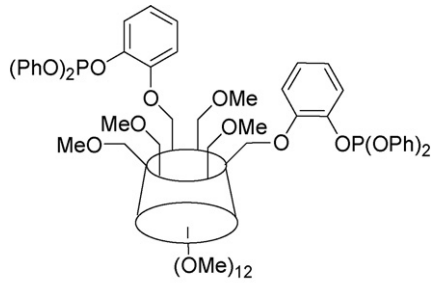


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Fig. 12. Diphosphite ligand **29**.

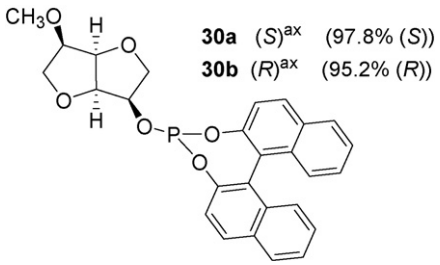


Fig. 13. Monophosphite ligands **30**. In brackets, the enantioselectivities obtained in the Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate are shown as examples.

ric hydrogenation. Research in this area was initiated by Reetz and coworkers. In connection with the previously described diphosphite ligands derived from D-mannitol **18**, they found that the related monophosphite ligands **30** provided similar enantioselectivities (Fig. 13) [29].

Following this work, the groups of Reetz et al. [30] and Chen and coworkers [31] have developed new efficient monophosphite ligands for the Rh-catalyzed asymmetric hydrogenation of vinyl carboxylates, dehydroaminoacids and enamides (Fig. 14). In particular, Reetz et al. also reported the use of ligands **31**–**35** in the Rh-catalyzed hydrogenation of vinyl carboxylates [30]. The results show that there is a cooperative effect between the configuration of the binaphthyl moieties and the configuration of the sugar backbone. Therefore, enantioselectivities were best with phosphite **31b**, prepared from (*R*)-binol and a D-(+)-glucose derivative (ee's up to 94%).

On the other hand, Chen and coworkers have successfully used ligands **31**–**32** and **36**–**39** in the Rh-catalyzed hydrogenation of dehydroaminoacids (ee's up to 98.4%) and enamides (ee's up to 99.6%) [31]. The hydrogenation results indicate that the enantiomeric excess depends strongly on the configuration of carbon atom C-3. In general, therefore, ligands **32** and **37** with an *R* configuration produced much higher enantioselectivity than ligands **31** and **36** with the opposite configuration. In this case, their results also suggest that there is a cooperative effect between the configuration of the binaphthyl moieties and the configuration of the carbohydrate backbone. The enantioselectivities (up to 99.6% ee) were therefore best with ligands **32b** and **37b**. Ligands **38** and **39** were also highly efficient in the hydrogenation of dehydroaminoacids and enamides providing high enantioselectivities (ee's up to 99.8%) and activities (TON up to 5000) [31c,d].

2.2. Heterodonor ligands

Several types of heterodonor carbohydrate ligands have been developed for application in asymmetric hydrogenation catalysis. In particular, phosphine–phosphite, phosphite–phosphoroamidite, phosphite–oxazoline and phosphinite-thioether ligands have produced excellent results.

2.2.1. Heterodonor P–P′ ligands

The first reports on the use of heterodonor P–P′ ligands were the phosphine-phosphonite ligand **40** [32], derived from D-mannitol,

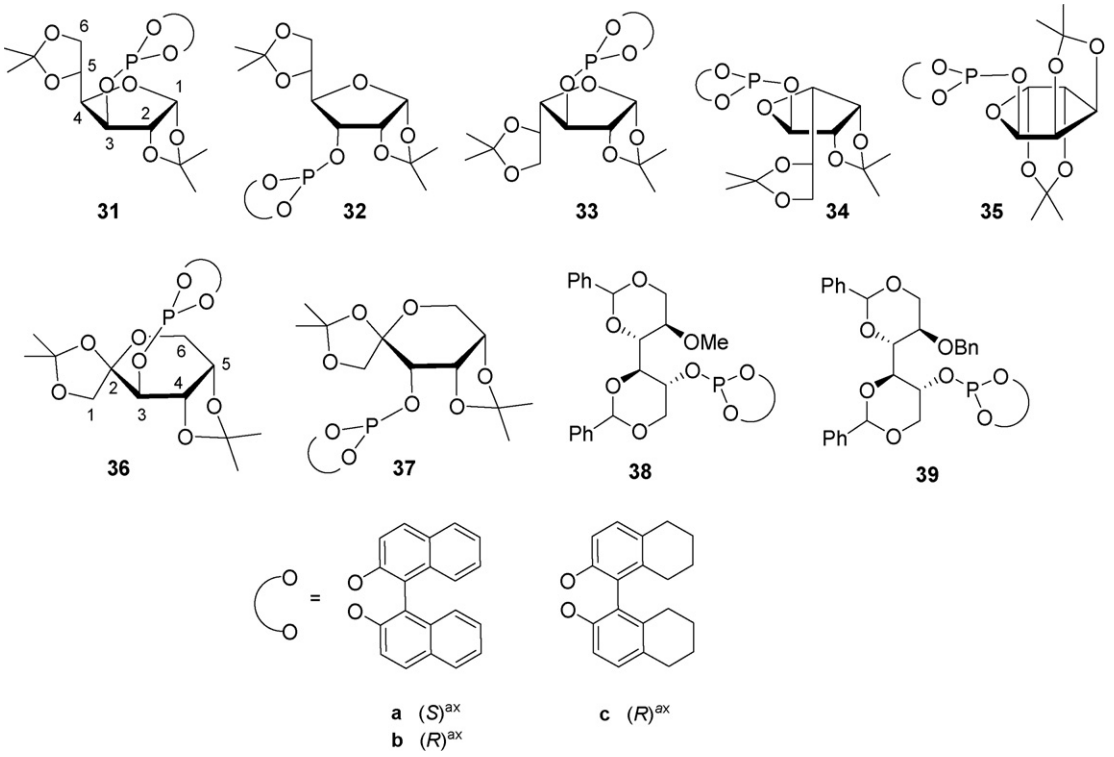


Fig. 14. Monophosphite ligands **31**–**39**.

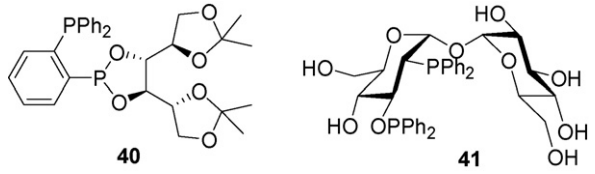


Fig. 15. Heterodonor P–P′ ligands **40** and **41**.

and phosphine-phosphinite ligand **41** [33], derived from L-α,α-trehalose (Fig. 15). These ligands were tested in the Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate and enamides, respectively, with moderate enantioselectivities (ee's up to 73%).

The first successful family of P–P′ carbohydrate ligands were the xylofuranoside phosphine–phosphite ligands **42** (Fig. 16) [34]. They were applied in the Rh-catalyzed asymmetric hydrogenation of several α,β-unsaturated carboxylic acid derivatives (ee's up to >99%) under very mild conditions. These ligands contain different phosphite substituents (**a**–**e**) that affect the catalytic performance. Therefore, the enantioselectivity was best with ligand **42b**, which contains bulky *tert*-butyl groups in the *ortho* and *para* positions of the biphenyl moiety. The results also indicate that the stereogenic binol units control the preferential enantiomer configuration. Therefore ligand **42d** with the *R*-binaphthyl moiety mainly provides the *R*-configuration of the hydrogenation product (97.6% ee), while ligand **42e** with the *S*-binaphthyl moiety gave the opposite enantiomer in 98.3% ee. Both enantiomers of the product can therefore be obtained with high enantioselectivity.

The second successful family of P–P′ donor carbohydrate ligands were the phosphite–phosphoroamidite ligands **43** and **44**, also derived from D-xylose (Fig. 16) [35]. These ligands are related to diphosphite ligands **19**–**20** and phosphine–phosphite ligands **42** (mentioned above). The introduction of a phosphoroamidite moiety at C-5 of the ligand backbone is highly adventitious, leading to high enantioselectivities in the Rh-catalyzed hydrogenation of dehydroaminoacids (ee's up to 99% using ligand **43b**).

The last family of mixed P–P′ donor carbohydrate ligands are the phosphinite-phosphite ligands **45** related to **25**–**26** in which a phosphinite moiety has been replaced by a phosphite group (Fig. 16). Ligand **45f** proved to be effective in the Ir-catalyzed hydrogenation of ketimines (ee's up to 73%) [21b,36].

2.2.2. Heterodonor P–N ligands

To the best of our knowledge, there is only one example of sugar-based P,N-ligands applied to the asymmetric hydrogenation. This includes the application of a pyranoside phosphite–oxazoline ligand library (**46**–**49**) in the Ir-catalyzed hydrogenation of unfunctionalized olefins (Fig. 17) [37]. These ligands can be easily tuned by variation in the oxazoline and in the biaryl phosphite moieties. By carefully selecting the ligand components high activities and enantioselectivities (ee's up to >99%) were obtained for several *E*- and *Z*-trisubstituted and 1,1-disubstituted olefins.

2.2.3. Heterodonor P–S ligands

Concerning the use of heterodonor P,S-sugar-ligand derivatives, phosphinite thioethers **50**–**52** (Fig. 18) have been successfully used in the asymmetric Rh-catalyzed hydrogenation of enamides and dehydroaminoacids (ee's up to 98%) [38,39]. Ligands **50**–**51** were developed having in mind the pseudo-enantiomers strategy used earlier by RajanBabu (ligands **7** and **8**). Therefore, although both ligands are from the readily available D-series, they acts as a pseudo-enantiomers providing access to both enantiomers of the hydrogenation products.

3. 1,2-Addition of nucleophiles to C=O and C=NR

The origin of sugar-ligand use in enantioselective 1,2-organometallic additions to π-systems can be traced to the pioneering work of Hafner and Duthaler [40]. Simple diacetalglucose as a ligand in the stoichiometric reaction of $CpTi(CH_2CH=CH_2)$(**53**-H)$_2$ with PhCHO affording the derived homoallylic alcohol in 90% (*R* configuration) (Fig. 19). Use of tartrate-based TADDOL ligands allowed the attainment of both *Re* and *Si* face additions to a range of aldehydes in high ee values (86–90%). However, attempts to extend this early precedent to reactions employing a catalytic amount of sugar-ligated Lewis acid and a terminal allyl source have met with limited success. Typically, such transformations have instead been restricted to directing group effects engendered by sugar-derived starting materials [41]. Recently, Appelt and Braga have introduced a very simple system composed of Sn or Zn metal in the presence of either saccharose (**54**) and especially β-cyclodextrin (**55**). Under these conditions allylbromide and aromatic aldehy-

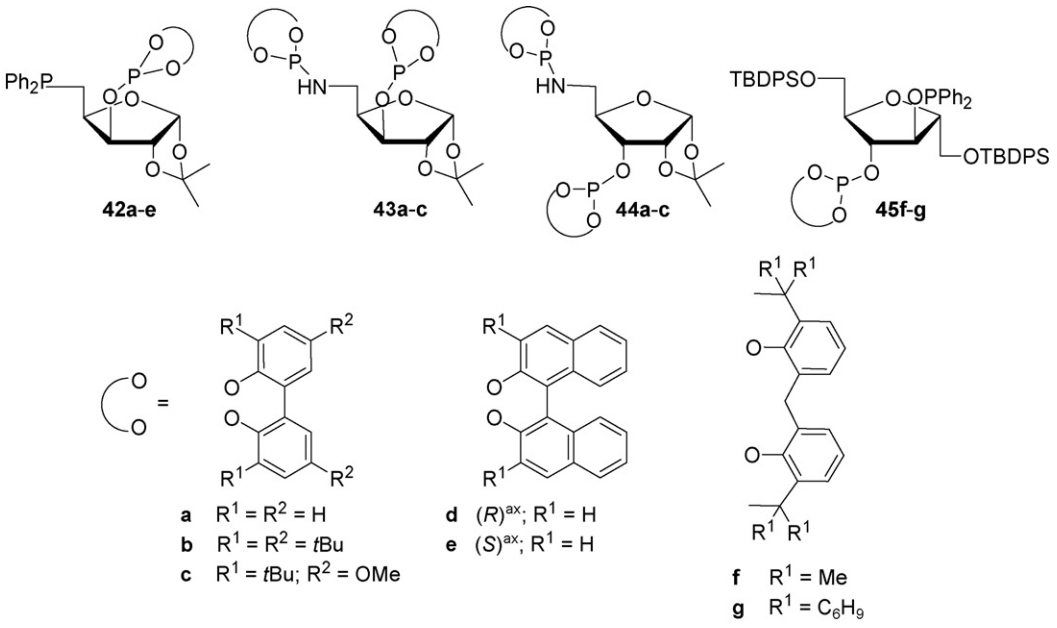


Fig. 16. Heterodonor P–P′ ligands **42**–**45**.

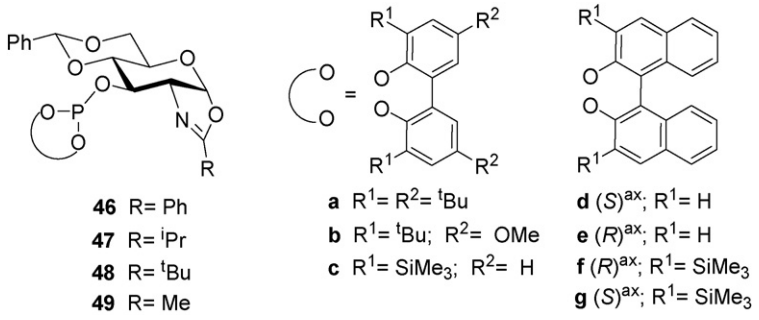


Fig. 17. Pyranoside phosphite–oxazoline ligands **46**–**49** derived from D-glucosamine.

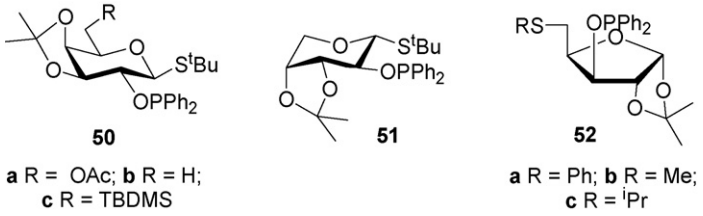


Fig. 18. Phosphinite-thioether ligands **50**–**52**.

des provide interesting levels of enantioselectivity (ee 62–90%) of the alcohol product even though presently high levels of catalyst loading are required (50–100 mol%) [42].

Given the ubiquitous nature of the reaction of $ZnEt_2$ and benzaldehyde to provide PhCH(Et)OH in very high ee value for a very wide range of ligands [43], it is perhaps surprising that sugar-based promoters are poorly represented in this field. Two potential reasons for this may be: (i), the potential for additional Zn···O contacts at the periphery of the ligand (as opposed to the desired, selective, 1,2-aminoalcohol motif); and (ii), the potential for zinc Lewis acid triggered ligand destruction leading to non-selective background reactions. Such problems are perhaps exemplified in Davies' heroic optimization to ligand structure **56** from a family of >30 sugar-derived aminoalcohols (Fig. 20) [44]. Even rigorous molecular mechanic and factorial analyses of the ligand parameters led to a process providing only 65% ee. Very closely related **57** provided 97% ee for the same transformation *provided* $Ti(iOPr)_4$ was present. The later is known to provide a 'cleaning' role in $ZnEt_2$ addition chemistry sequestering away undesired alkoxide products. Zheng obtained intermediate results (79–82% ee) for $ZnEt_2$ addition to ArCHO using **58**–**59** derived from D-fructose.

Recently, much greater success has been attained in the 1,2-addition of *in situ* formed RC≡CZn(OTf) to aldehydes and imines (Carreira's conditions [45]). By using the β-anomer of **56** Davies could now attain highly selective alkynation of a range of aliphatic aldehydes (95–99+% ee) that were proposed to be attained from transition state **60** (Fig. 21) [46]. However, aromatic aldehydes proved unreactive in this chemistry or provided Canizzaro by-products. Conversely, aromatic imines were cleanly alkynated in the presence of $Cu(OTf)\cdot 1/2C_6H_6$ (5 mol%) and glucosamine-derived **61** (8 mol%) with good stereoselectivities (80–99% ee) for a small range of aromatic substituents [47]. However, in some cases low catalytic activity was encountered—apparently the reaction conditions were not tried on the equivalent aliphatic substrates.

Although in many cases the addition of ZnR_2 (R = Et or higher homologues) is known the equivalent 1,2-methyl additions can prove problematic. In general, Zn–Me bonds (ca. 68 kcal mol^{-1} (285 kJ mol^{-1}) [48]) are significantly stronger than their higher partners and this can lead to sluggish reactivity. These problems can be overcome by the use of $AlMe_3$ reagents where the reactions are driven by the formation of a very strong Al–O bond (~140 kcal mol^{-1} (590 kJ mol^{-1})). One particularly attractive variant is to use the air stable reagent $[DABCO](AlMe_3)_2$ **62** in the presence of Ni-phosphite catalysts. A range of sugar-derived phosphites has been screened in this chemistry of which **31d**, **63** and **48a** were the most successful, **31d** being the best (Fig. 22) [49].

For nucleophiles other than organometallics the most significant advances are perhaps the TMSCN additions of Shibasaki which have been extensively summarized in reviews by this group (Fig. 23) [50]. These additions utilize **64**, which was originally attained from (D)-glucose. However **64**, and related analogues have recently also been attained by direct asymmetric ligand synthesis.

In the case of formation of **65** the stereoselectivity of the reaction can be reversed by changing the gadolinium catalyst to a titanium system using $Ti(OiPr)_4$ [51]. Excellent enantioselectivities are realised in both cases. However, the equivalent aliphatic ketones show significantly lower ee values (40–76% ee) due to their poorer steric profiles. The equivalent TMSCN additions to ketimines require the presence of a protic additive, hindered phenols being the best, to achieve effective catalyst turnover to **66** [52]. Ligand **64** is also active in the opening of meso aziridines [53] and some conjugate addition processes [54] which are presented

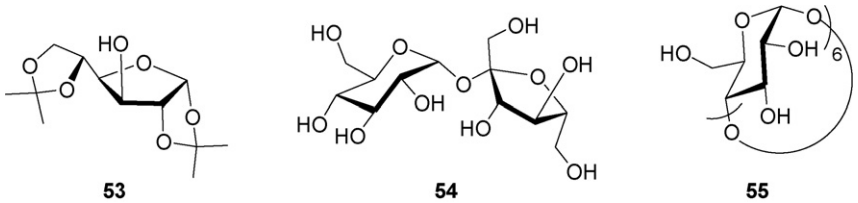


Fig. 19. Carbohydrate promoters for asymmetric allylation.

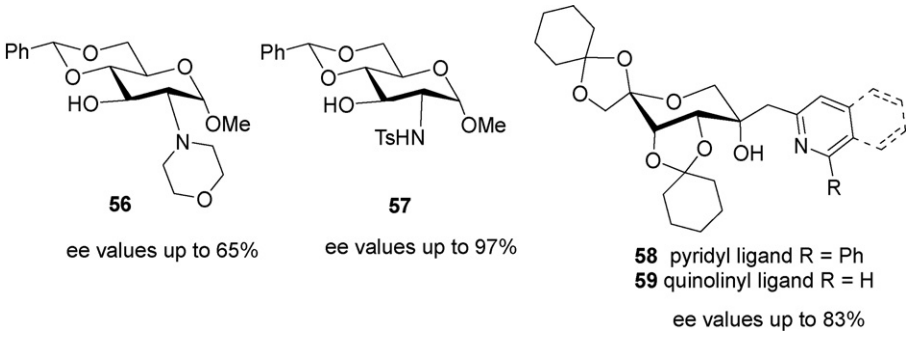


Fig. 20. (Amino)sugar-derived ligands for the 1,2-addition of $ZnEt_2$ to aromatic aldehydes.

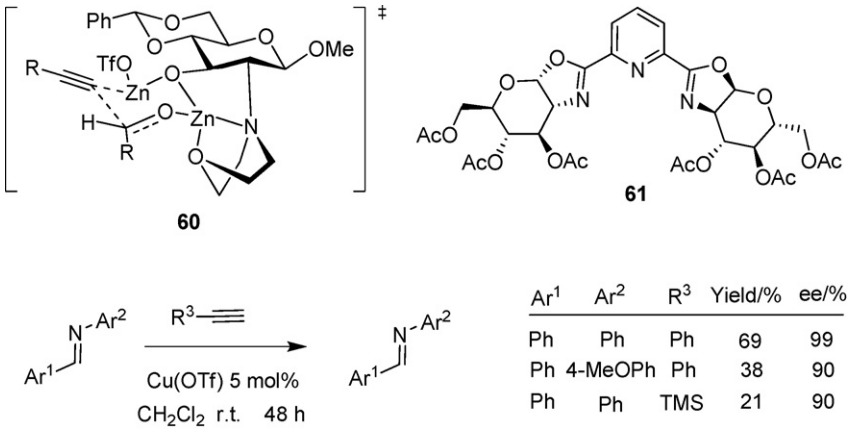


Fig. 21. Asymmetric alkynylation of aldehydes and imines.

here for completeness (Fig. 23). Finally, a recent new application of sugar-ligated ruthenium complexes has been identified: catalytic hydrolysis of nitriles (Fig. 24). Presently the activities are modest and there have been no attempts to desymmetrize meso dinitriles [55].

4. 1,4-Addition of nucleophiles to Michael acceptors

Spescha was the first to report the use of glucose derived **68** (Fig. 25) to demonstrate copper-catalyzed Asymmetric Conjugate Addition (ACA) of BuMgCl to cyclohexenone in 1993 [56]. The relative low levels of asymmetric induction realised (46–50% ee) can be attributed to the possibility of geometrically diverse polar Mg···O contacts. Organometallics of more covalent M···O bonding character lead to greater rigidity in enantiodetermining step, leading in turn, to the more selective catalysts. Commonly, AlR_3 reagents are employed at −20 to −40 °C using 2–5 mol% of ligated Cu^I catalysts, while the less reactive ZnR_2 species require significantly higher temperatures (0–25 °C) to attain complete substrate conversions. Recent contributions to this field are summarized in Table 1 with the associated ligand structures given in Fig. 25.

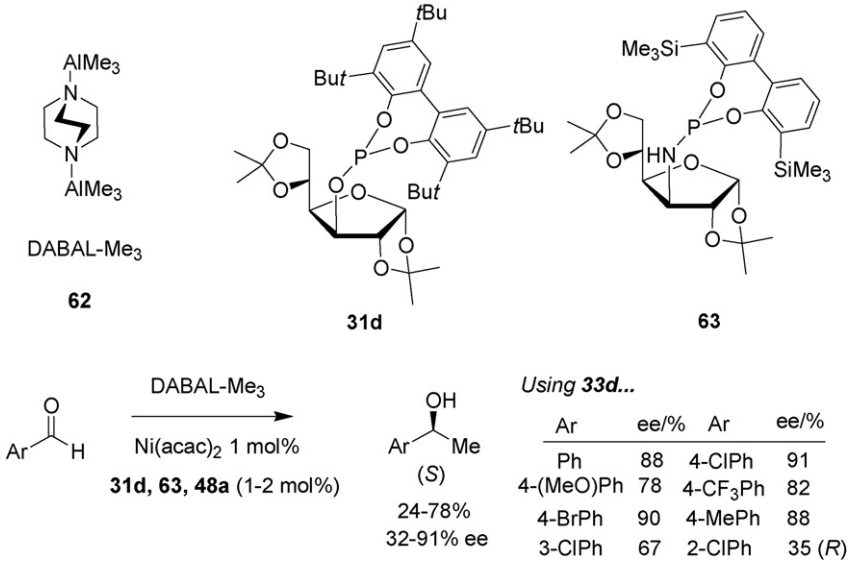


Fig. 22. Ni-catalyzed asymmetric 1,2-additions of **62** to aromatic aldehydes.

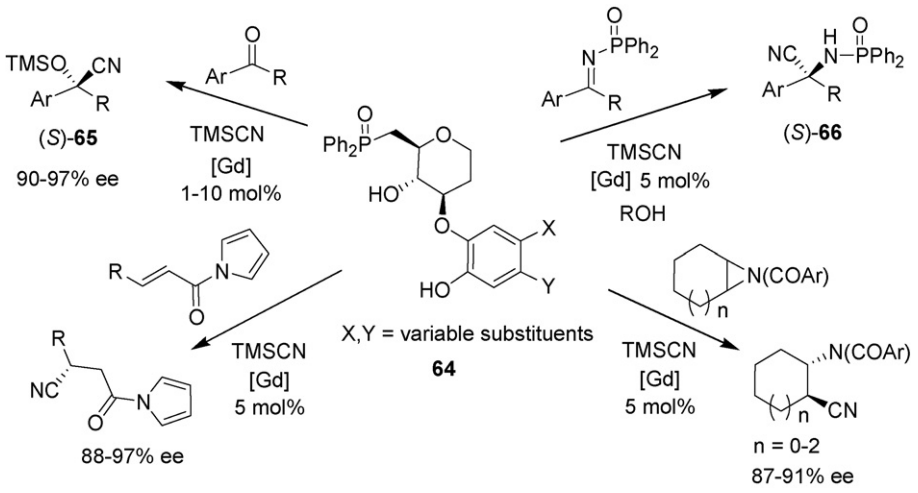


Fig. 23. Catalytic asymmetric reactions of TMSCN promoted by **64**; [Gd] is $Gd(OiPr)_3$.

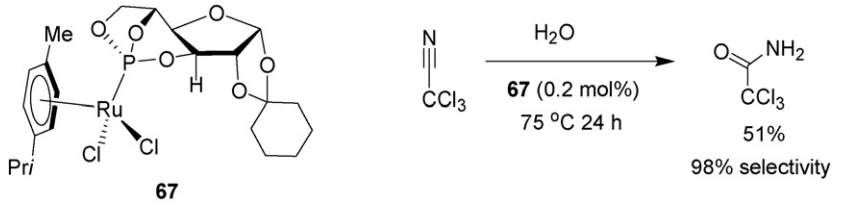


Fig. 24. Chemoselective nitrile hydrolysis.

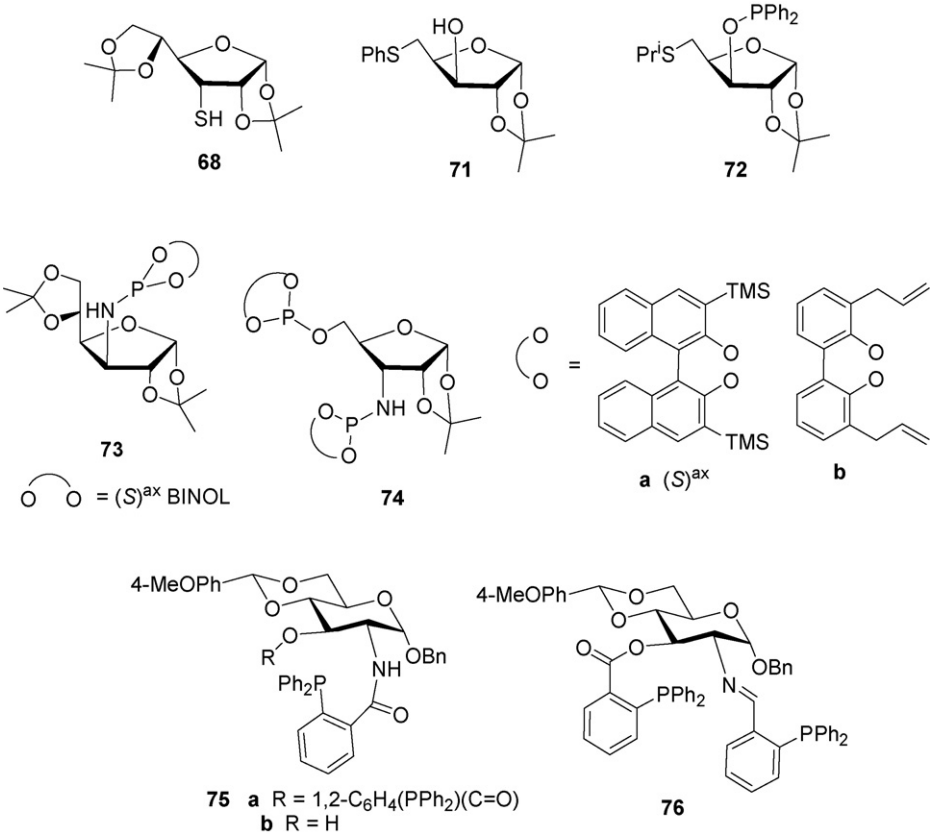
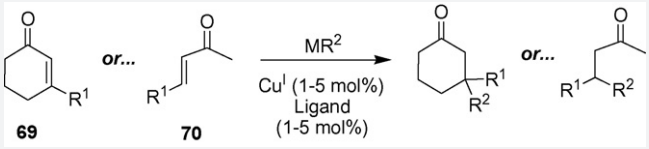


Fig. 25. Sugar ligands used in 1,4-addition of organometallics to Michael acceptors.

Table 1
Copper-catalyzed ACA reactions of Michael acceptors.



Substrate	R^1	MR^2	Ligand	Yield/%	ee/%	References
69	H	BuMgX	**68**	>90	46–50	[56]
69	H	$ZnEt_2$	**21g**	98	84	[57]
69	H	$ZnEt_2$	**71**	92	60	[58]
69	H	$ZnEt_2$	**72**	63	72	[59]
69	H	$AlEt_3$	**31b**	77	48	[60]
70	C_5H_{11}	$AlMe_3$	**31b**	51	48	[60]
69	H	$AlMe_3$	**73**	88	56	[61]
69	H	$ZnEt_2$	**74a**	94	84	[62]
69	Me	$AlEt_3$	**74b**	52	90	[62]
70	C_5H_{11}	$AlMe_3$	**74a**	51	79	[62]
69	H	$AlEt_3$	**46d**	61	64	[63]
70	C_5H_{11}	$AlMe_3$	**46d**	85	62	[63]
70	Pr^i	$AlMe_3$	**46d**	90	80	[63]
70	C_5H_{11}	$ZnMe_2$	**75a**	70	95	[64]
70	C_5H_{11}	$ZnEt_2$	**75a**	80	91	[64]
70	C_5H_{11}	$ZnMe_2$	**75b**	78	61	[64]
70	C_5H_{11}	$ZnMe_2$	**76**	75	92	[64]
70	Pr^i	$ZnMe_2$	**75a**	47	89	[64]
70	Pr^i	$ZnMe_2$	**76**	33	94	[64]

While the exact mechanism of the addition of AlR_3 or ZnR_2 species to enones under Cu^I/L^* catalysis is not fully understood it is popularly assumed that effective two-point binding of the catalyst to the enone is required to attain a selective transition state. Phosphino-sugar ligands can be helpful in this respect as they are somewhat predisposed to bind the additional 'hard' (Al or Zn) Lewis acids necessary for carbonyl coordination through the presence of multiple O-donor sites. In general, the enantioselectivities associated with 1,2-CMe_2-protected furanoside ligands derived from D-glucose or xylose are modest (ee values up to ~60%), particularly if the phosphorus is attached with the *xylo* configuration ('up') at C_3. Ligands with an inverted configuration at this centre have provided more successful catalyst (i.e. **74**). Similar advantages have been noted in the use of amino sugars, especially those derived from glucosamine (**46d**, **75**, and **76**). Again, while the exact coordination mode of these ligands remains unknown, the reverse of stereochemical induction provide strong evidence of O-Zn coordination in the catalyst derived from **75b**. Use of **75a** or **76** allowed for highly stereoselective additions of ZnR_2 (R = Me, Et) across a range of demanding acyclic aliphatic enones.

Rhodium-catalyzed ACA of aryl boron reagents has become the definitive method for the preparation of 3-aryl ketones and other closely related species. Although use of chiral diene ligands dominate this area, Boysen [3,47,122] has recently demonstrated the viability of the P,C=C ligand **77** in 1,4-additions of $PhB(OH)_2$ (Fig. 26).

While not strictly within the remit of this review, very recently Shao has introduced glucose derived **78** in organocatalyzed Michael chemistry to nitro acceptors (Fig. 27) [65]. The role of the sugar unit is not clear: the chirality of the diamine sub-unit dictated the enantioface of the nitroalkene attacked and no sugars other than D-glucose were used. Ligand **78** is of interest as thiocarbonyl compounds have proved of use in Cu^I-catalyzed additions of $AlMe_3$ to enones [66]. In a similar vein, the D-glucose derived crown ether **79** promotes phosphonate 1,4-addition to a range of substrates, in the presence of NaO*t*Bu, of which nitriles were the most effective (Fig. 27) [67]. The organocatalytic area has also provided an initial example of a sugar-decorated carbene ligand (**81**) [68]. Although not isolable in this case it could be entrapped as its Pd(II) complex showing a Pd-$C_{carbene}$ bond length of 1.990 Å. While the latter complex has not yet been used in catalysis, the free ligand was despite its fragility active in catalytic conjugate umpolung chemistry affording a mixture of **82a**–**b** (with the former being the major epimer). No comment was made on the enantioselectivity in this process.

5. C–C cross-coupling

5.1. Pd-allylic substitution

The Pd-catalyzed asymmetric allylic substitution, which involves the attack of diverse nucleophiles at an allylic metal intermediate or S_N2'-type allylic substitution, is one of the most versatile routes for preparing optically active compounds [4d,69]. Besides a high level of asymmetric induction, the advantages of this method are its tolerance of a wide range of functional groups and a great flexibility in the type of bonds that can be formed.

Most of the successful ligands reported to date for this process have been designed using three main strategies. The first was the use of a secondary interaction of the nucleophile with a side chain of the ligand to direct the approach of the nucleophile to one of the allylic terminal carbon atoms [70]. The second was to increase the ligand's bite angle in order to create a chiral cavity in which the allyl system is perfectly embedded. This idea paved the way for the successful application of ligands with large bite angles for the allylic substitution of sterically undemanding substrates [4d,69,71]. A third final strategy was the use of heterodonor ligands that result in an electronic discrimination of the two allylic terminal carbon atoms due to the different *trans* influences of the donor groups [4d,69,72]. This made it possible to successfully use a wide range of heterodonor ligands (mainly P,N-ligands) in allylic substitution reactions [4d,69]. More recently, the introduction of biaryl-phosphites into the ligand design has emerged as a new strategy [73]. The benefits of this latter strategy are: (1) substrate specificity decreases because the chiral pocket created is flexible enough to enable the perfect coordination of hindered and unhindered substrates [74], (2) reaction rates increase thanks to the

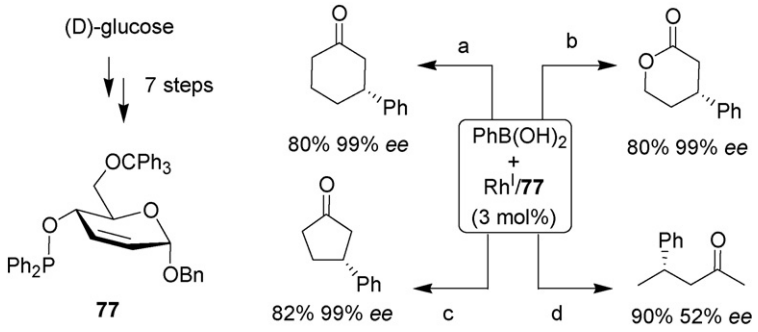


Fig. 26. Rhodium(I)-**77** catalyzed additions of $PhB(OH)_2$ to various enones: (a) cyclohexenone; (b) 5,6-dihydro-2H-pyran-2-one; (c) cyclopentenone; (d) penten-2-one.

larger π-acceptor ability of these moieties [75], and (3) regioselectivity towards the desired branched isomer in monosubstituted linear substrates increases thanks to the π-acceptor ability of the phosphite moiety that enhances the S_N1 character of the nucleophilic attack [76].

Carbohydrate-based ligands have only recently shown their huge potential as a source of highly effective chiral ligands in the Pd-catalyzed asymmetric allylic substitution reactions. Several types of ligands, mainly heterodonors, have been developed for this process and some of the results are among the best ever reported. In the next section we summarize the most relevant catalytic data published for the Pd-catalyzed allylic substitution with carbohydrate-based ligands.

5.1.1. Homodonor ligands

5.1.1.1. Phosphine ligands. Unlike asymmetric hydrogenation process, few diphosphines have provided good enantioselectivities in allylic substitutions [4d,69]. In this respect, one of the most versatile ligands for this process is the diphosphine **83** developed by Trost (Fig. 28) [69c,77]. The remarkable properties of this ligand are related to the bite angle, which is larger than in unstrained Pd-diphosphine complexes. Consequently, the P-aryl groups generate a chiral cavity, in which the allyl system is embedded, and this provides high ee's for several sterically undemanding substrates.

Regarding the use of carbohydrate-based diphosphine ligands only two contributions have appeared. In 2000, the previously mentioned C_1-furanoside diphosphine ligands **3**–**5** (Fig. 3) were applied in the Pd-catalyzed asymmetric allylic substitution reactions with moderate success (ee's up to 78%) [78].

In 2006, Ruffo and coworkers developed a modification of the Trost-bis(phosphinoamides) ligands **83** using diamines based on glucose and mannose as chiral auxiliaries (Fig. 28, ligands **84a** and **85**) for the highly enantioselective Pd-catalyzed desymmetrization of meso-cyclopenten-2-ene-1,4-diol biscarbamate (ee's up to 97%) [79]. Interestingly both enantiomers of the product can be obtained in high enantioselectivities by switching from glucose (**84**)

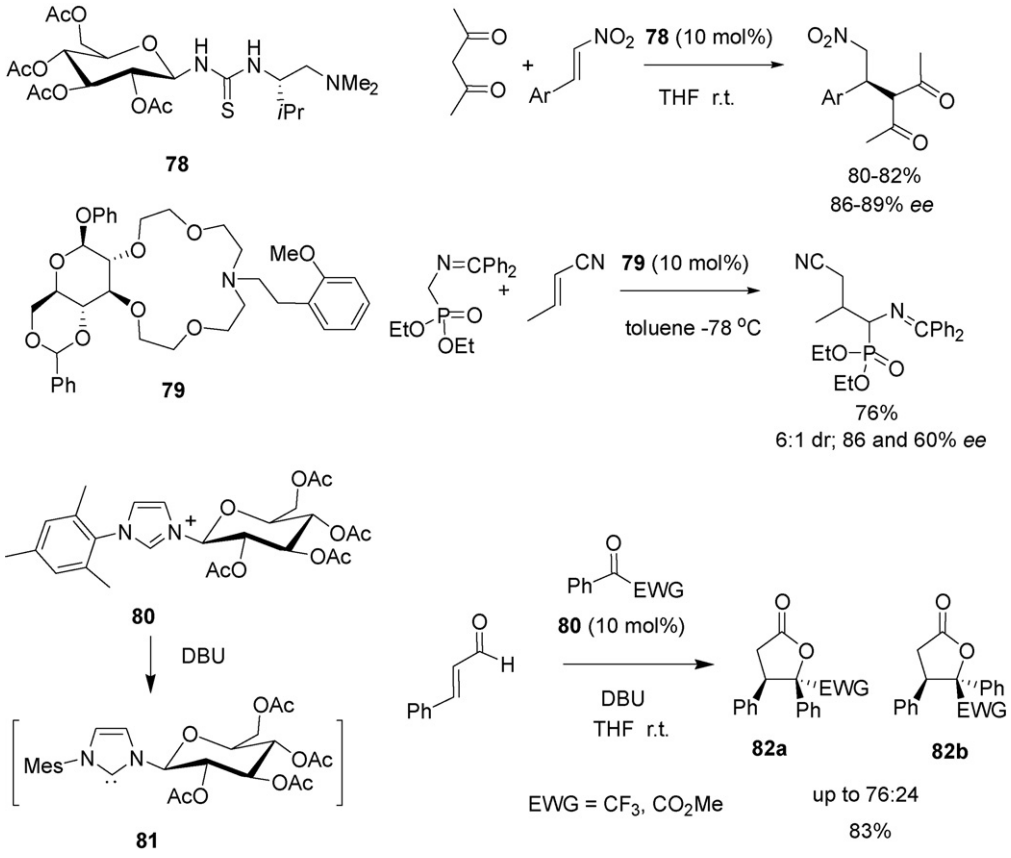
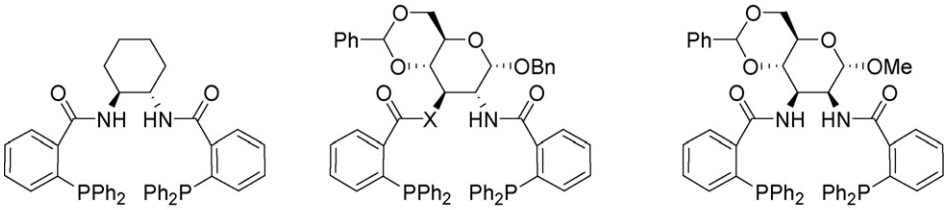


Fig. 27. Emerging organocatalytic conjugate additions.



83 **84a** X= NH **84b** X= O **85**

Fig. 28. Bis(phosphinoamides) **83**–**85**.

to mannose (**85**) derivative ligands. Ligand **84b**, derived from glucosamine, provided improved enantioselectivities in this process (ee's up to 98%). Moreover, it provided promising results under multiphase homogeneous conditions.[80] Recently, a bipyridine derivative, related to **84a**, have provided high regio- (up to 98%) and enantioselectivities (up to 99%) in the Mo-catalyzed allylic alkylation of monosubstituted substrates [81].

5.1.1.2. Phosphinite ligands. The use of phosphinite ligands has been scarce and with little success. Therefore, the previously reported pyranoside diphosphinite **7** (Fig. 5) [82] and furanoside diphosphinites **13** and **14** (Fig. 7) [83] provided low-to-moderate enantioselectivities (ee's up to 59%).

5.1.1.3. Phosphite ligands. A review of the research into carbohydrate-based phosphite ligands reveals three main ligand types. The first one represented an important breakthrough in the use of phosphite ligands for this process. It showed the successful application of the previously furanoside diphosphite ligands **19**–**24** (Fig. 10) in the Pd-catalyzed allylic substitution of dimethyl malonate and benzylamine to several acyclic and cyclic allylic esters (Fig. 29) [1c,75b,78a,84]. These excellent results are in line with the presence of a π-acceptor flexible bulky biphenyl phosphite moiety that allows the creation of a more flexible chiral pocket which is able to control the size of the chiral pocket as required by each substrate type and, therefore, obtain high enantioselectivities. Although, high rates and enantioselectivities were achieved in the Pd-catalyzed allylic substitution of monosubstituted substrates, the regioselectivity for the branched products was not high.

Enantioselectivities were best with ligand **22b**, which has a glucofuranoside backbone and bulky *tert*-butyl substituents at both *ortho* and *para* positions of the biphenyl moieties. Ligand **19b** was also used to stabilize Pd-nanoparticles. These particles catalyzed the allylic alkylation of *rac*-1,3-diphenylprop-2-enyl acetate with dimethyl malonate leading to an almost total conversion of the (*R*) enantiomer and almost no reaction with the (*S*). This gives rise to 97% ee for the alkylation product and a kinetic resolution of the substrate recovered with ca. 90% ee [85].

The second report appeared in 2005 and reported the application of the previously mentioned C_2-diphosphite ligands **18** (Fig. 9) in the Pd-catalyzed allylic alkylation of several acyclic and cyclic allylic esters with low success (ee's up to 41%) [86].

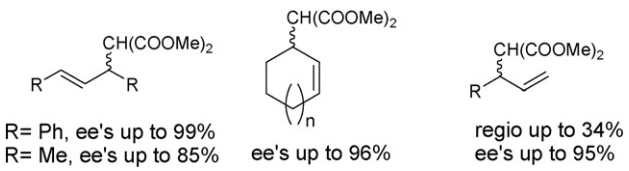


Fig. 29. Acyclic and cyclic allylic esters tested with ligands **19**–**24**.

The third report appeared more recently and described the successful application of the previously mentioned **25**–**28** ligands (Fig. 11) in the Pd-catalyzed allylic substitution reaction of 1,3-diphenylprop-2-enyl acetate [75c]. Ligand **25b** provided high activity (TOFs > 22000 h^{-1}) and excellent enantioselectivities (ee's up to 99%).

5.1.1.4. Phosphoroamidite ligands. During the last decades, there has been a huge advance in the use of phosphoroamidite ligands for several asymmetric processes [87]. However, to best our knowledge only one family of diphosphoroamidite ligands **86** based on carbohydrates has been successfully applied in asymmetric catalysis (Fig. 30) [74c]. Good-to-excellent activities (TOF's up to 850 for the allylic alkylation of *rac*-1,3-diphenylprop-2-enyl acetate with dimethyl malonate) with enantioselectivities up to 95% have been obtained in the Pd-catalyzed allylic alkylation for several di- and monosubstituted linear and cyclic substrates. The results indicate that catalytic performance is highly affected by the substituents and the axial chirality of the biaryl moieties of the ligand. The study of the 1,3-diphenyl and cyclohexenyl Pd-π-allyl intermediates indicates that the nucleophilic attack takes place predominantly at the allylic terminal carbon atom located *trans* to the phosphoroamidite moiety attached to C-5.

5.1.1.5. S-donor ligands. Sulfur donor ligands have been used much less than phosphorus ligands in this process because a mixture of diastereomers can be obtained upon coordination of the thioether ligand to the metal, which can lead to a decrease in stereoselection if the relative rates of the intermediates are similar. Despite this, high enantiomeric excesses have been achieved [88]. In this context, Khiar and coworkers used a combinatorial approach to find the best dithioether ligand **87** from a library of 64 potential ligands (Fig. 31) for the Pd-catalyzed allylic alkylation of dimethyl malonate to 1,3-diphenylprop-2-enyl acetate (ee's up to 90%) [89a]. In the search for both enantiomers of the alkylation product, the authors successfully prepared pseudo-enantiomers **88** and **89** derived from D-galactose and D-arabinose, respectively (Fig. 31) [89b].

5.1.2. Heterodonor ligands

5.1.2.1. P–P′ ligands. The first successful family of P–P′ carbohydrate ligands were the phosphite–phosphoroamidite ligands **43** and **44** (Fig. 16) and ligands **74** and **90** (Fig. 32), derived from D-xylose. They were successfully applied in the Pd-asymmetric allylic substitution (ee's up to 98%) [90]. Interestingly, this ligand family also provides high activity (because of the high π-acceptor capacity of the phosphoroamidite moiety) and enantioselectivities in different substrate types (mono- and disubstituted linear and cyclic substrates). The previously related phosphine–phosphite ligands **42** (Fig. 16) with a furanoside backbone have been also used in the model enantioselective Pd-catalyzed allylic alkylation and amination substitutions reactions providing up to 42% and 66% ee, respectively [84b].

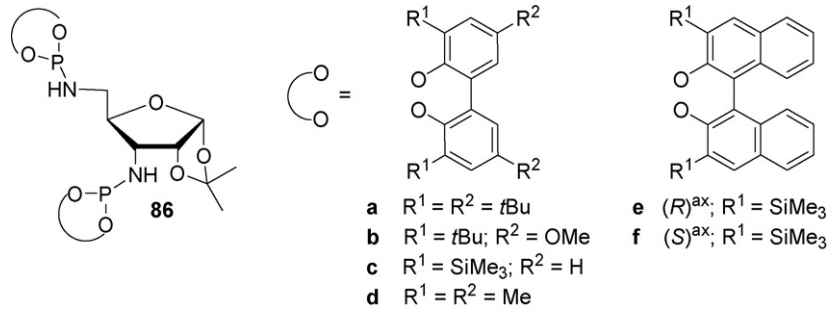


Fig. 30. Furanoside diphosphophoroamidite ligands **86**.

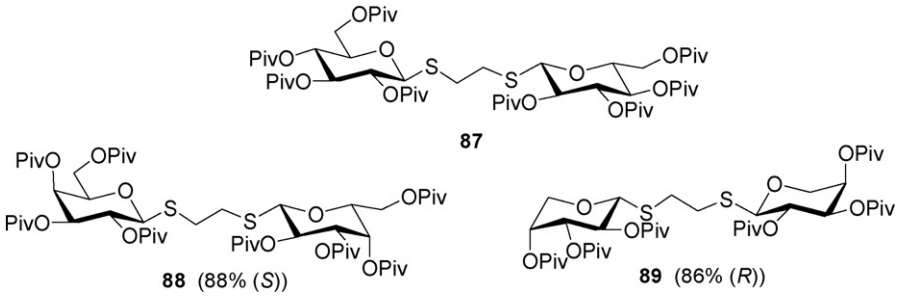


Fig. 31. Dithioether ligands **87**–**89**. The maximum ee values reached are also shown in brackets.

Recently, the phosphite–phosphoroamidite ligands **91** with pyranoside backbone (Fig. 32) have been developed for the Pd-catalyzed allylic substitution reaction of several substrates. Enantioselectivities up to 89% have been obtained for disubstituted linear and cyclic substrates [91].

5.1.2.2. P–N ligands. Several types of P,N-donor carbohydrate ligands have been developed for use in Pd-asymmetric allylic substitutions (Fig. 33).

In particular, many phosphorus-oxazoline ligands have produced excellent results. In this context, ligand **92** derived from D-glucosamine was successfully applied in the Pd-catalyzed allylic alkylation of dimethyl malonate to symmetrically and non-symmetrically substituted allyl acetates (Fig. 33) [92]. These results are in line with a nucleophilic attack *trans* to the phosphorus atom.

Phosphinite-oxazoline ligands **95** also derived from D-glucosamine provided high enantioselectivity in the 1,3-diphenylprop-2-enyl acetate, but enantioselectivities were low-to-moderate for unhindered linear and cyclic substrates [93,94]. The results of the allylic alkylation of dimethyl malonate to 1,3-diphenylprop-2-enyl acetate indicated that the best enantioselectivity was obtained with the smallest substituent on oxazoline (R = Me, ligand **95a**). Their results also indicate that the nucleophilic attack took place *trans* to the phosphorus atom thought and *endo* π-allyl Pd-intermediate.

Recently, the replacement of the phosphinite group in ligands **95** by a phosphite moiety led to the formation of phosphite–oxazoline ligands **46**–**49** (Fig. 17) [95]. The introduction of a biaryl phosphite moiety in the ligand design proved to be highly adventitious. Therefore, the new ligands **46**–**49** provided higher enantioselectivities

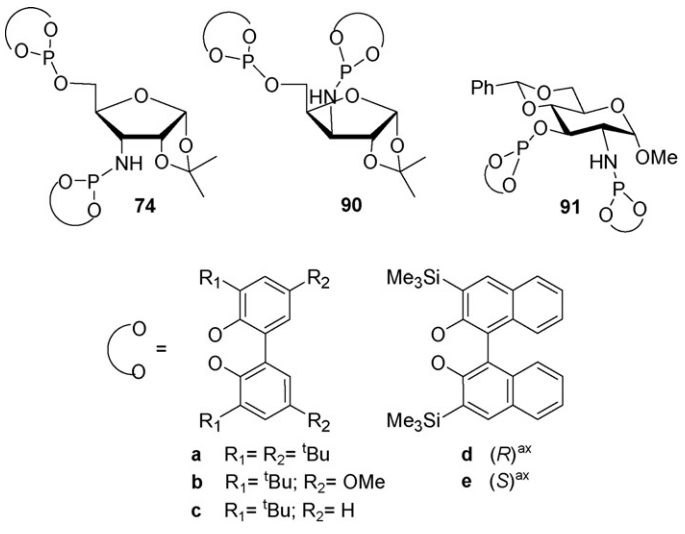


Fig. 32. Phosphite–phosphoroamidite ligands **74**, **90** and **91**.

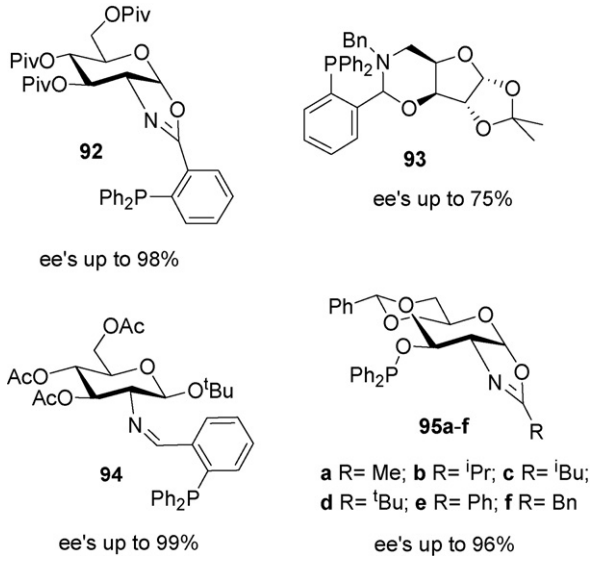


Fig. 33. Representative P,N-ligands.

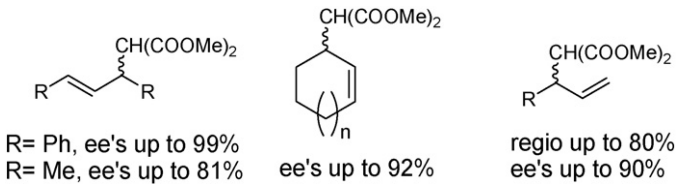


Fig. 34. Acyclic and cyclic allylic esters tested with ligands **46**–**49**.

and reaction rates than related phosphinite-oxazoline ligands in the allylic substitution (ee's up to 99%). Moreover, the presence of a flexible phosphite moiety opens up the possibility of using the Pd-phosphite–oxazoline catalytic systems to a wide range of different substrate types in this catalytic process (Fig. 34). These ligands were also used to stabilize Pd-nanoparticles [96].

Other P,N–donor carbohydrate ligands, such as phosphine-oxazine ligands **93** [100] and phosphine-imine ligand **94** [97] has also been developed for the Pd-catalyzed allylic substitution of 1,3-diphenylprop-2-enyl acetate (Fig. 33).

5.1.2.3. P–S ligands. Several combinations of P,S-donor ligands have been studied. In particular, the phosphine-thioether, phosphinite-thioether and phosphine-oxathiane have proven to be effective in enantioselective Pd-catalyzed allylic substitutions (Fig. 35).

Among the phosphine-thioether, it should be noted that ligands **96** [98], **98** [99] and **100** [100] can provide enantioselectivities up to 94% in the palladium-catalyzed allylic substitution reactions.

More recently, the previously mentioned furanoside phosphinite-thioether ligands **52a**–**c** (Fig. 18) have been extended by the introduction of more substituents with different electronic and steric properties on the thioether moiety (ligands **52d**–**g**, Fig. 40). Ligands **52** were applied in the Pd-catalyzed allylic substitution of mono- and disubstituted linear and cyclic substrates (ee's up to 95%) [101].

At the same time, the previously mentioned phosphinite-thioether ligands **50** and **51** with pyranoside backbones (Fig. 18) were successfully applied in Pd-catalyzed allylic substitution of 1,3-diphenylprop-2-enyl acetate (ee's up to 96%). Enantioselectivities were best when bulky *tert*-butyl substituents were present in the thioether moiety. Both enantiomers of the allylated products were obtained by using pseudo-enantiomeric ligands **50** and **51** [38a,102].

5.1.2.4. P–O ligands. Phosphine-amide ligands **101**–**106** (Fig. 36) with pyranoside backbone have been extensively studied for the Pd-catalyzed allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate [97c,103]. The results clearly showed that enantioselectivity is highly affected by the configuration of the anomeric carbon, the chelate ring size formed upon coordination to Pd and the rigidity of the ligand. Therefore, ligands **101**, **105** and **106** that forms a six-membered chelate ring and with a β anomeric carbon afforded higher enantioselectivities than ligands **102** (with an α anomeric carbon) and **104** (that forms a seven membered chelate ring). Moreover, the results between ligands **105** and **106** indicate a cooperative effect between stereocenters that resulted in a matched combination for ligand (*S*)-**105**.

5.1.2.5. N–S ligands. Thioglucose-derived ligands **107**, containing a chiral oxazoline moiety (Fig. 37), when used as ligands in the palladium-catalyzed allylic alkylation of diphenylprop-2-enyl acetate have provided some of the best results achieved in this reaction with mixed N,S-donor ligands [104].

More recently, the pyranoside thioether-imine ligand **108** (Fig. 37), related to **98**, was applied in the allylic alkylation of 1,3-diphenylprop-2-enyl acetate with low enantioselectivity [99a].

5.2. Heck reaction

The asymmetric Heck reaction generally referred to the palladium mediated coupling of aryl or vinyl halides or triflates with alkenes in the presence of base has become one of the most versatile methods for C–C bond formation (Scheme 2). This process has found extensive applications in asymmetric synthesis. Shibasaki and Overman have convincingly demonstrated the value of such transformation in the synthesis of complex natural molecules [4d,105].

The bulk of the reported examples involve intramolecular reactions, which have the advantage of allowing easy control of alkene regiochemistry and geometry in the product [105g]. In contrast, successful intermolecular reactions have until very recently been limited to quite reactive substrates, principally O-, N-heterocycles, which again simplifies the question of alkene regiochemistry [4d,105]. It should be noted that in the asymmetric intermolecular Heck reaction it is not only the enantioselectivity of the process

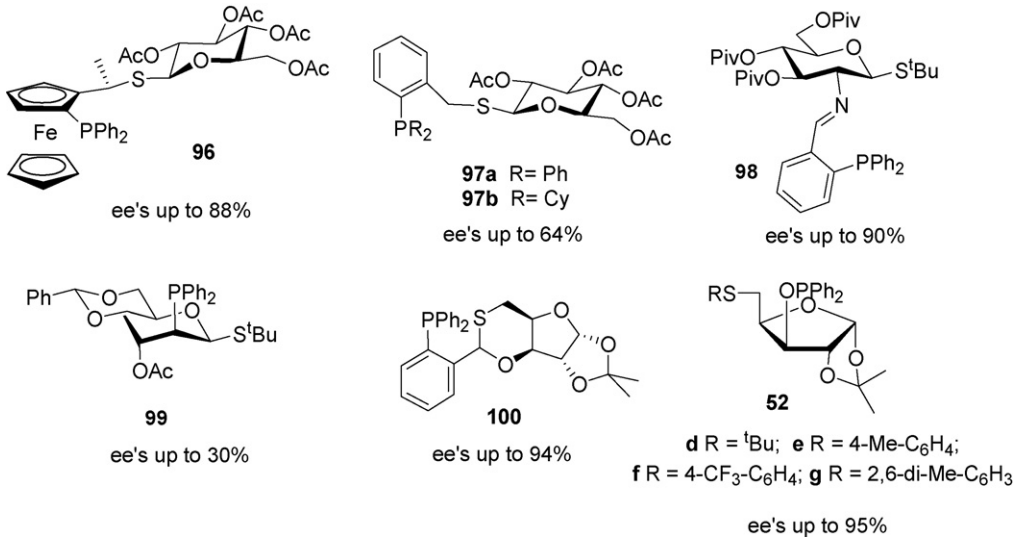


Fig. 35. Representative P–S ligands.

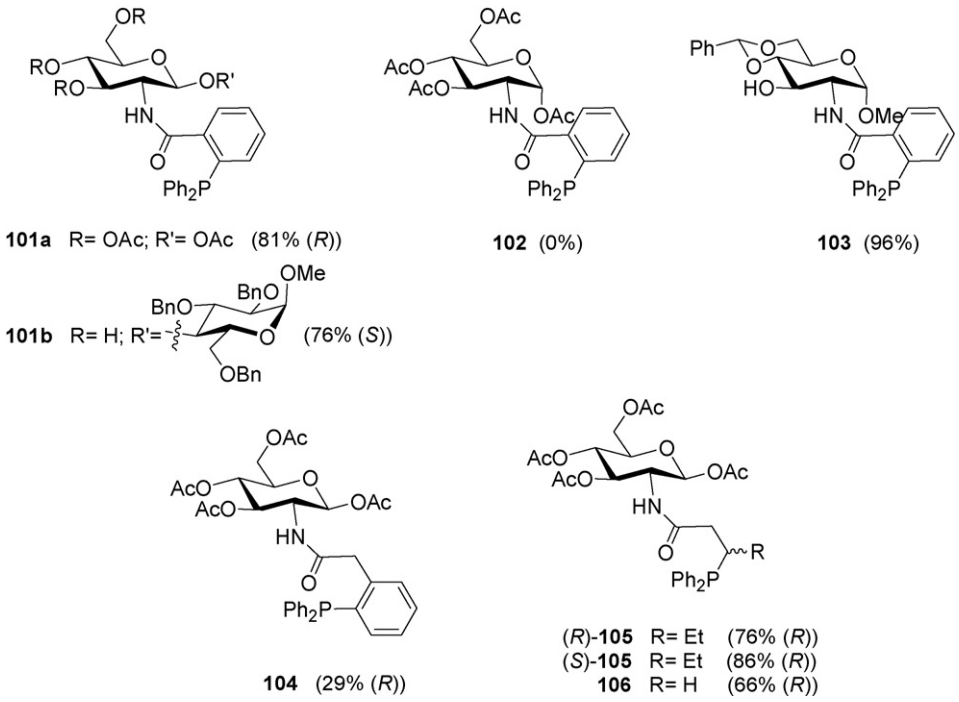
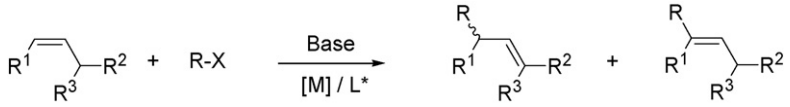
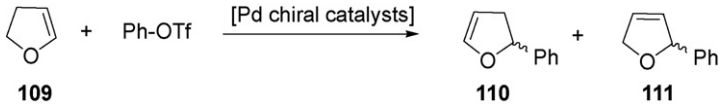


Fig. 36. Phosphine-amide ligands **101**–**106**. The enantioselectivities for 1,3-diphenylprop-2-enyl acetate are also shown in brackets.

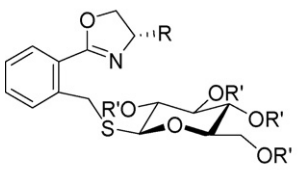


Scheme 2. Pd-catalyzed Heck reaction. X = halide or triflate.



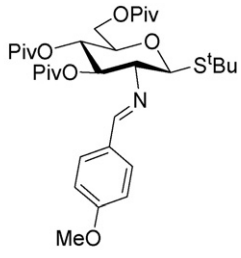
Scheme 3. Model Pd-catalyzed intermolecular Heck reaction.

that needs to be controlled, the regioselectivity is also a problem, because a mixture of regioisomers can be obtained. So, for example, in the Heck reaction of 2,3-dihydrofuran **109** with phenyl triflate, a mixture of two products is obtained: 2-phenyl-2,3-dihydrofuran **110** and the expected 2-phenyl-2,5-dihydrofuran (**111**; Scheme 3). The former is formed due to an isomerization process [4d,105].



107a-d

	R	R'	% ee
a	^{i}Pr	C(O)Me	93 (*S*)
b	^{i}Pr	C(O)^{t}Bu	97 (*S*)
c	Ph	C(O)Me	90 (*S*)
d	Ph	C(O)^{t}Bu	96 (*S*)



108

ee's up to 34%

Fig. 37. Representative N–S ligands.

5.2.1. Ligands

Diphosphines, which have played a key role in the success of the intramolecular version, were early applied. Among these, the Pd-BINAP were the first catalytic system that offered good regio- (in favour to product **110**) and enantiocontrol [4d,105]. In the last few years, a class of heterodonor ligands – the phosphorous-oxazoline – have emerged as suitable ligands for the intermolecular Heck reaction of several substrate types and triflates sources [106]. In contrast to Pd-BINAP systems, they offer preferentially isomer **111** in high enantioselectivities.

Although carbohydrate-based ligands have been successfully used in other enantioselective reactions, there are only two reports on the highly enantioselective palladium-catalyzed asymmetric Heck reaction using this type of ligand [106m,p,q].

The first successful application of carbohydrate-ligands in this process used the pyranoside phosphinite-oxazoline ligands **95** (Fig. 33) in the Pd-catalyzed enantioselective arylation of 2,3-dihydrofuran (ee's up to 96%). The results indicated that enantioselectivity was hardly affected by the type of oxazoline substituents. This set of ligands were also applied in the phenylation of *trans* and *cis*-crotyl alcohols with low enantioselectivity (ee's up to 17%), representing the first example of the enantioselective intermolecular

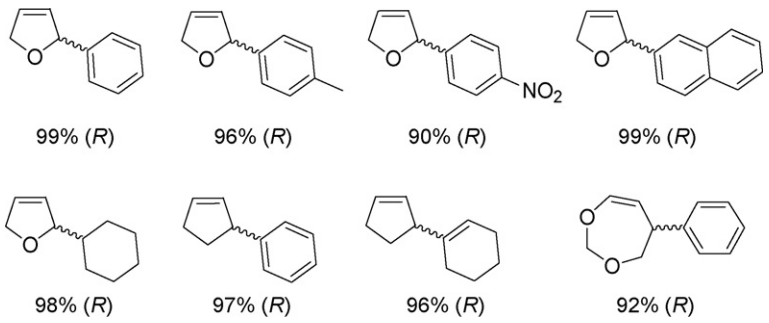


Fig. 38. Representative results obtained with ligands **46**–**49**.

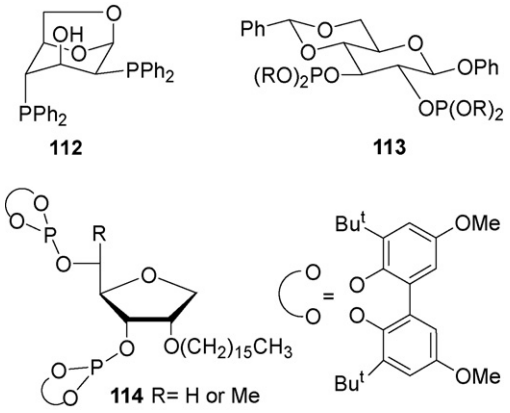


Fig. 39. Ligands **112**–**114**.

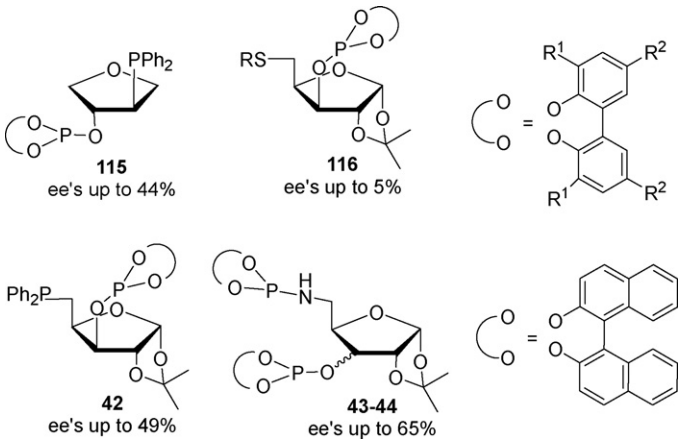


Fig. 40. Heterodonor ligands in asymmetric hydroformylation.

arylation of prochiral alkenes [106m]. The authors also disclosed by isolation of the arylpalladium complex [(*p*-$MeO_2CC_6H_4$)PdI(**95a**)] and the stoichiometric reactions of the complex [PhPd(**95f**)]OTf with 2,3-dihydrofuran the mechanistic aspect for Mizoroki–Heck-type reaction using P,N-ligands. They found out that the deprotonation at β-position with a base leading to an alkene–(2-phenyl-2,5-dihydrofuran)–palladium(0) complex is responsible for the selective formation of the product.

Recently, the previously mentioned phosphite–oxazoline ligands **46**–**49a**–**g** (Fig. 17) were also successfully applied in the Pd-catalyzed asymmetric Heck reaction of several substrates and triflate sources [106p,q]. The results indicates that the degree of isomerization and the effectiveness in transferring the chiral information in the product and the activity can be tuned by correctly choosing ligand components (phosphite and oxazoline substituents).The introduction of a biaryl phosphite moiety in the ligand design proved to be highly adventitious. Therefore, excellent activities (up to 100% conversion in 10 min), regio- (up to >99%) and enantioselectivities (ee's up to 99%) were obtained in a wide range of substrates and triflate sources (Fig. 38).

6. Hydroformylation

Asymmetric hydroformylation has attracted much attention as a potential tool for preparing enantiomerically pure aldehydes [107]. Despite its importance, asymmetric hydroformylation is under-

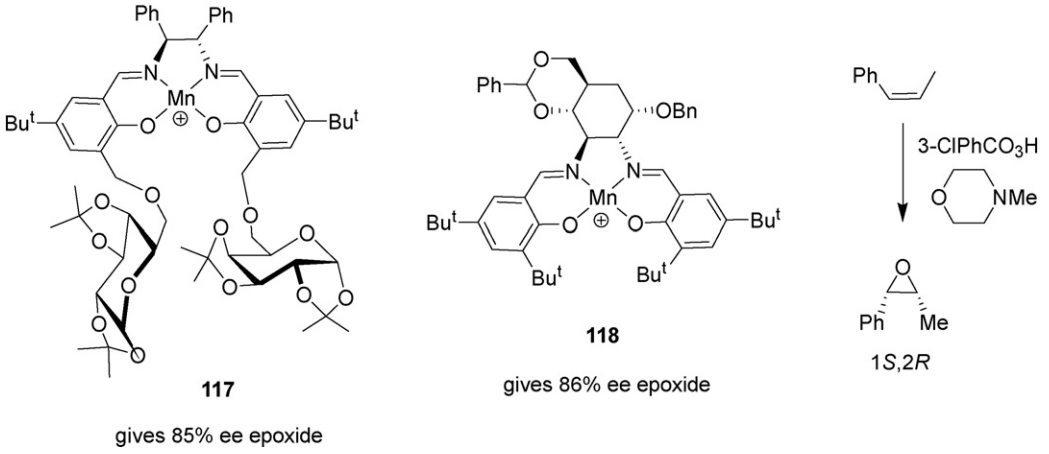


Fig. 41. Carbohydrate-based ligands in the epoxidation of (*Z*)-β-methylstyrene.

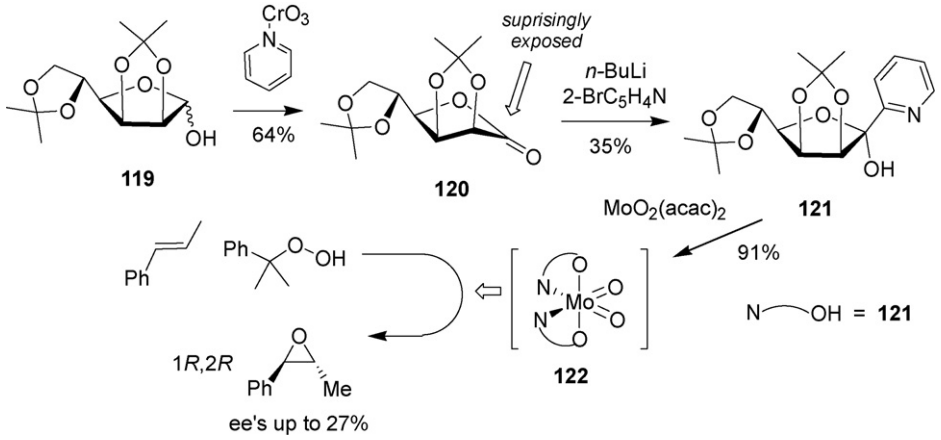


Fig. 42. Stereospecific synthesis of epoxidation pre-catalyst **122**.

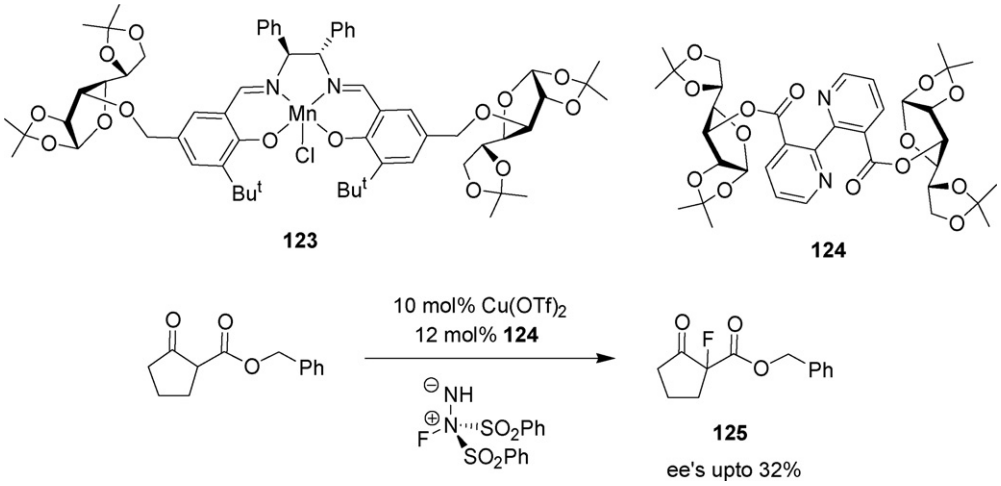


Fig. 43. Other reactions of salen and bipyridyl-based sugar ligands.

developed compared to other processes such as hydrogenation. Traditionally, vinylarenes have been the most studied substrates. Although, Rh-diphosphites and Rh-phosphine–phosphite BINAPHOS-type (BINAPHOS = (2-(diphenylphosphino)-1,1′-binaphthalen-2′-yl)-(1,1′-binaphthalen-2,2′-yl)phosphite) have proved to be the most efficient catalytic systems [2,108], recently, diphospholane [109], bis-(diazaphospholodine) [110] and phosphine-phosphoroamidite [111] have emerged as suitable alternative ligands for this process. The use of these latter ligands has allowed the successful Rh-catalyzed hydroformylation of other type of substrates, like allyl cyanide, vinyl acetate and some bicyclic olefins [109,110,111].

6.1. Homodonor ligands

As far as carbohydrate diphosphine ligands are concerned, only two families of ligands (**3**–**5** and **112**) were developed early on [112]. It should be noted that excellent enantioselectivities were obtained using ligand **112** (Fig. 39) in the hydroformylation of vinyl acetate.

The use of carbohydrate diphosphinite ligands in asymmetric hydroformylation has also been scarce [113]. Therefore, the previously mentioned ligands **7**, **13** and **14** have been applied in the asymmetric hydroformylation of several vinylarenes with enantioselectivities up to 72%.

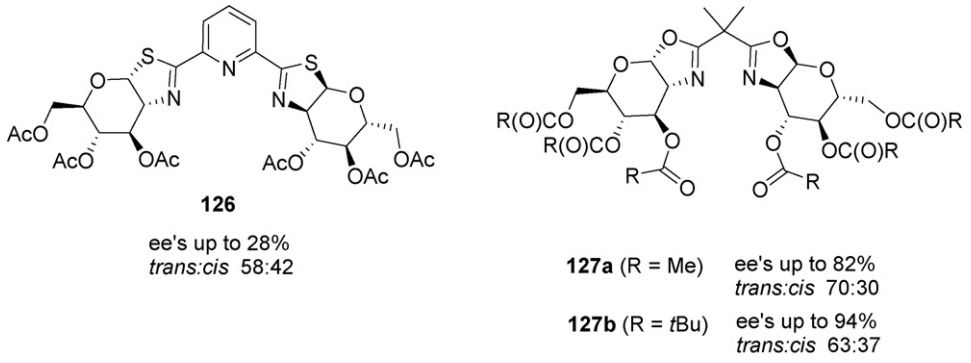


Fig. 44. Glucosamine-derived ligands for cyclopropanation.

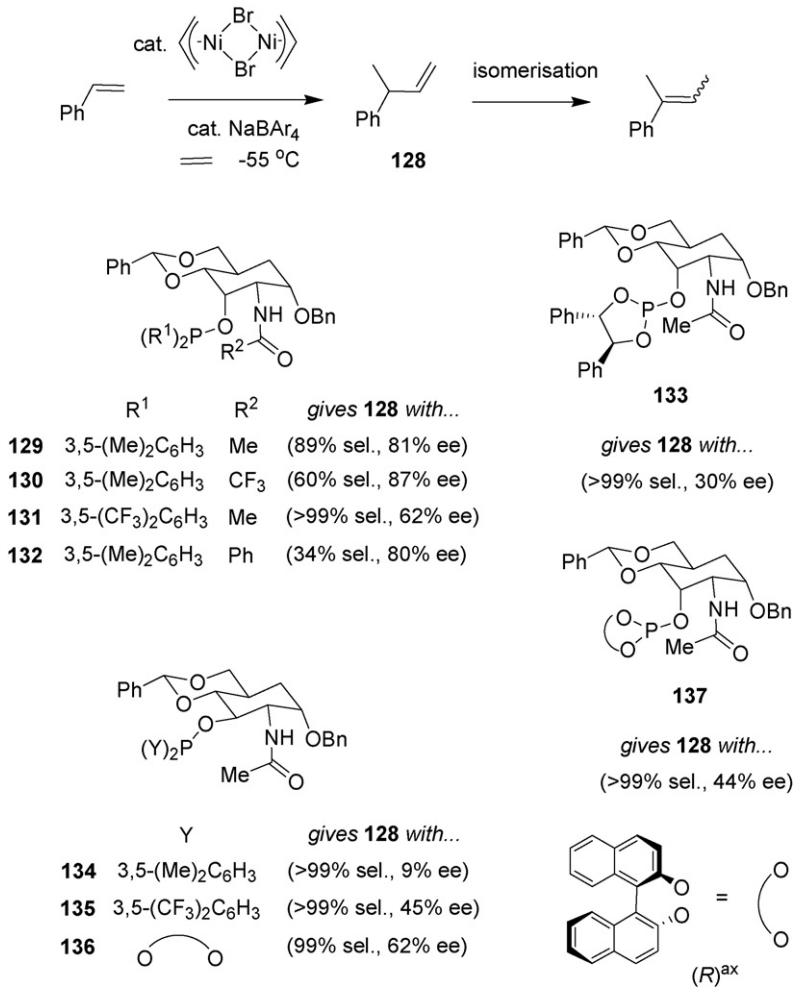


Fig. 45. Hydrovinylation and carbohydrate ligands used. The numbers in the parentheses are the selectivity to the 3-phenylbutene **128** and its ee value respectively.

Concerning, carbohydrate diphosphite ligands only three families have been applied. The early use of diphosphite ligand **113** (Fig. 39), with β-D-glucopyranoside backbone, proceed with moderate success (ee's up to 36%) [23]. An important breakthrough in this area came with the use of the previously mentioned tunable furanoside diphosphite ligands **19–24** in the Rh-catalyzed hydroformylation of vinyl arenes [114]. These ligands show both excellent enantioselectivities (up to 93%) and regioselectivities (up to 98.8%) under mild conditions. More recently, these ligands were also successfully applied in the Rh-catalyzed asymmetric hydroformylation of more challenging substrates: heterocyclic olefins [115]. Unprecedentedly high enantioselectivities for five-membered heterocyclic olefins (i.e. 2,3-dyhydrofuran, 2,5-dihydrofuran and *N*-acetyl-3-pirroline) were obtained (ee's up to 75%). Seven-membered heterocyclic dioxepines were also successfully hydroformylated with enantioselectivities (ee's up to 68%) among the best reported. In 2009, diphosphite ligands **19** and **22** were modified by replacing the 1,2-O-acetal by a simple alkyl chain attached to C-2 (ligands **114**, Fig. 39). However, this modification led to lower enantioselectivities [116]. The previously mentioned ligand **25** were also applied with moderate success in the Rh-catalyzed hydroformylation of vinylarenes (ee's up to 60%) [27].

6.2. Heterodonor ligands

Following the early success of the heterodonor BINAPHOS ligand in this process, several types of heterodonor carbohydrate ligands have been developed for application in the asymmetric hydroformylation catalysis but these have met with little success (Fig. 40) [117].

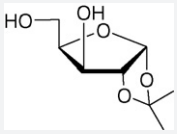
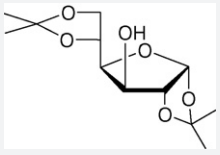
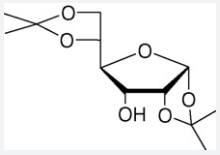
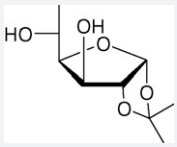
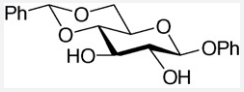
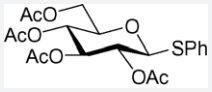
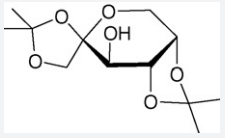
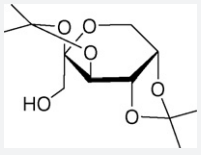
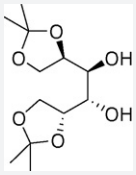
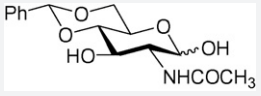
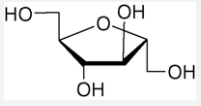
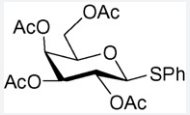
7. Other catalytic transformations

7.1. Oxidation

The use of sugar-based ligands in oxidation catalysis is a relatively recent development dating to 2002 [118]. Despite the obvious potential for ligand degradation many sugar decorated ligands appear relatively stable under oxidising conditions. Recently, in a screening of (*Z*)-β-methylstyrene epoxidation using sugar-functionalized salen ligands, Zhao found galactopyranose derived **117** to be the most effective (providing 85% ee epoxide) when using *m*-CPBA in the presence of *N*-methylmorpholine (used to suppress uncatalyzed epoxidation) (Fig. 41) [119]. In closely related chemistry Ruffo has used glucosamine-derived **118** in an identical transformation leading to the production of the epoxide with almost identical selectivity [120]. The similar nature of these two results suggest that the principal stereochemical determining motifs in these systems are the 'Jacobsen-like diamines' rather that the sugar peripheries.

In a nice example of stereoselective complex synthesis Herrmann and Kühn oxidised isopropylidene protected-D-mannofuranose **119** with CrO_3·pyridine to afford a good yield of ester **120**. This unexpectedly affords the more sterically congested

Table 2
List of key sugar backbones.

Product	Starting material[a]	References	Estimated price[b]
	D-Xylose (33 €/kg)	[128,129]	3.5 €/g (8.7 €/g)
	D-Glucose (9.5 €/kg)	[128]	0.9 €/g (1.2 €/g)
	D-Glucose (9.5 €/kg)	[128,130,131]	7 €/g (25 €/g)
	D-Glucose (9.5 €/kg)	[128,116]	30 €/g
	D-Glucose (9.5 €/kg)	[132–135]	8 €/g (39 €/g)
	D-Glucose (9.5 €/kg)	[132,136]	1.5 €/g (13 €/g)
	D-Fructose (27 €/kg)	[137]	1.5 €/g
	D-Fructose (27 €/kg)	[137,138]	1.5 €/g
	D-Mannitol (49.5 €/kg)	[139]	2.5 €/g (7.1 €/g)
	D-Glucosamine (177 €/kg)	[140,141]	9 €/g
	D-Glucosamine (177 €/kg)	[142]	5.5 €/g
	D-Galactose (150 €/kg)	[143,144]	2 €/g (14 €/g)

[a] In brackets are shown the commercial price.
[b] Estimated price making the desired precursor from the unprotected sugar at 0.2–0.5 mol scale without taking into account the electricity, waste disposal and salary costs. In brackets are shown averaged commercial prices.

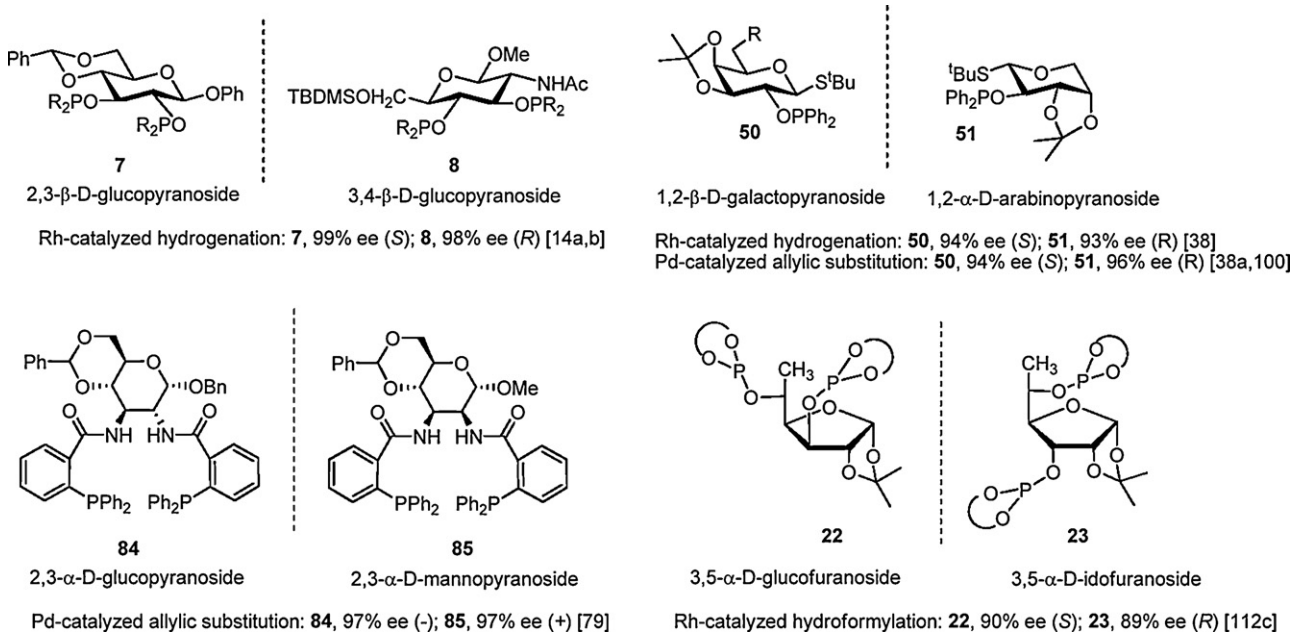


Fig. 46. Representative sugar cores for pseudo-enantiomeric ligand pairs.

diastereomer **119** in the presence of *in situ* generate 2-pyridyllithim (Fig. 42) [121]. The addition is proposed to take place from an envelope conformation that promotes addition to the *Re* face, although only 35% of **121** is isolated. Reaction of **121** with $MoO_2(acac)_2$ afforded **122** as a single Λ-chiral at metal complex that was crystallographically characterised. Unfortunately, while 1 mol% of **122** does catalyze (*E*)-β-methylstyrene (which is not a good substrate for **117**–**118** under normal conditions) using cumyl hydroperoxide, the maximum enantioselectivity attained was only 27%.

In related O-atom transfer reactions, 6-amino-6-deoxyglucopyranoside-based Schiff-base ligands and other carbohydrates have been used for vanadium-catalyzed peroxide-based sulfide oxidation. Enantioselectivities up to 60% were realised.[122] Aside from O-atom-transfer, sugar-based ligands have found recent use in oxidative kinetic resolution and also electrophilic fluorination (considering the latter as an oxidative process of an enolate). Thus in the first case, use of manganese pre-catalyst **123** (Fig. 43) in the presence of $PhI(OAc)_2$ allows the kinetic resolution of 1-phenylethanol with a selectivity factor of 11.2 [123]. At 60% conversion to acetopheneone the starting material is recovered with 89% ee. However, the major contribution to the selectivity of the catalyst was the diamine linker, not the sugar. In the second case (electrophilic fluorination), ligand **124** has been used to promote the formation of [(**124**)Cu('enolate')]$^+$ intermediates where the 'enolate' ligand is derived from the 1,3-dicarbonyl starting material. The electron-rich double bond of this species is intercepted by an achiral external F^+ source of which *N*-fluoro-bis-benzenesulfonylimide was found to be the best. Presently the optical yields in the carbohydrate ligands, exemplified by **124**, are similar to those seen with other more common *N*,*N*-chiral ligands, such as bis-oxazolines [124].

7.2. Cyclopropanation

The use of Cu^I catalysts in the presence of chiral *N*,*N*-ligands is well known to activate diazocompounds towards alkenes and promotion of the addition of $N_2{=}CH(CO_2Et)$ to styrene has become a standard 'test reaction' for the efficacy of new ligands. Recently, Boysen has introduced new *N*,*N*-chelates based on D-glucosamine (**126**–**127**) (Fig. 44) [125]. In general, these ligands do not offer any great advantages over pre-existing systems, similar selectivities are attained. The related thio ligand **126** delivers only modest (up to 28% ee) for the same test reaction. Ligands **127** fare better, especially when the pivolyl substituted variant is used. The enantioselectivities observed in these reactions mirror those seen in bis-oxazoline-based approaches. In particular, the same limitation is found in that diastereo (*cis*/*trans*) selectivity in these reactions is at best modest.

7.3. Hydrovinylation

Carbohydrate ligands have a proven track record of success in hydrovinylation since the first of these was introduced by Rajan-Babu and coworkers in 1994 [126]. The selectivities observed in these reactions are highly sensitive to substituent change. For example, inclusion of electron withdrawing substituents at the nitrogen substituents [$NR(CO)CF_3$] of these glucosamine-derived ligands led to more active isomerisation catalysts with nickel giving a depletion of the desired 3-arylbutene kinetic product **128**. A graphical summary of the ligands tried and the resultant selectivity is given in Fig. 45 [127]. For catalysts containing ligands **136** and **137** use of the diastereomeric $(S)^{ax}$ BINOL derived ligands led to mis-matched cases showing minimal enantioselectivity (2–19% ee).

8. Ligand structural features

As we have seen during this review, the structural diversity of carbohydrates and the high density of functional groups offer a wide variety of opportunities for derivatization and tailoring of synthetic tools in the search of the right ligand for each particular reaction [1]. The choice of sugar cores and functional groups is crucial and depends of the reaction to be studied. A selection of prominent sugar cores are shown in Table 2 (see Section 9). Several functional groups (mainly P and N donor groups, such as phosphine, phosphite, amides, oxazolines, etc. ...) can be attached to these basic sugar backbones.

In addition, another important feature of sugar-based cores is the rational design of pseudo-enantiomeric ligands thanks to their high modularity. Using this strategy both enantiomers of the

reaction product can be obtained without the use of expensive unnatural, prohibitively expensive L-carbohydrates. Fig. 46 shows some representative sugar cores for pseudo-enantiomeric ligand pairs.

9. Entry points to sugar-ligand design

To the non-carbohydrate specialist the preparation of novel sugar cores can seem a daunting task hindered by the polarity of the unprotected parents and wide reagent ranges or specialist conditions often required. However, a wide range of starting materials are commercially available of which a selection of the most important are given in Table 2 together with their approximate relative costs (2010 figures). To make use of sugar as chiral ligands in asymmetric catalysis in organic media, one should increase the solubility of the sugars polyols by protecting some of the hydroxyl groups. One of the more easy ways to do that is the use of cyclic acetals (such as isopropylidene and benzylidene). The use cyclic acetals is usually preferred over non-cyclic protecting groups since they reduce the conformational mobility of the sugar ring, which is beneficial in the transfer of the chiral information to the product outcome. Moreover, for the preparation of sugar backbones one usually has to take advantage of the rich repertoire of the protecting group chemistry available. Because the protecting groups are introduced and removed under different conditions, a large plethora of partially protected carbohydrate cores are available. Table 2 also gives, in our opinion, the most useful compilation of key starting material precursors with their corresponding references [128].

References

[1] Key major reviews:
(a) M. Diéguez, O. Pàmies, C. Claver, Chem. Rev. 104 (2004) 3189;
(b) M. Diéguez, O. Pàmies, A. Ruiz, Y. Diaz, S. Castillón, C. Claver, Coord. Chem. Rev. 248 (2004) 2165;
(c) M. Diéguez, A. Ruiz, C. Claver, Dalton Trans. (2003) 2957;
For a more recent review concentrating on ligand donor type in the period (up to 2006) see:
(d) M. Diéguez, C. Claver, O. Pàmies, Eur. J. Org. Chem. (2007) 4621.

[2] C. Claver, O. Pàmies, M. Diéguez, in: A. Borner (Ed.), Phosphorus Ligands in Asymmetric Catalysis, vol. 2, Wiley-VCH, Weinheim, 2008, p. 506.

[3] M.M.K. Boysen, Chem. Eur. J. 13 (2007) 8649.

[4] See for instance:
(a) I. Ojima (Ed.), Catalytic Asymmetric Synthesis, 2nd ed., Wiley-VCH, Weinheim, 2000;
(b) B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, 2nd ed., Wiley-VCH, Weinheim, 2002;
(c) H.U. Blaser, E. Schmidt (Eds.), Asymmetric Catalysis on Industrial Scale: Challenges, Approaches and Solutions, Wiley-VCH, Weinheim, 2004;
(d) E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, vols. 1–3, Springer-Verlag, Berlin, 1999;
(e) R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994.

[5] O. Pàmies, M. Diéguez, G. Net, A. Ruiz, C. Claver, J. Chem. Soc. Dalton Trans. (1999) 3439.

[6] (a) U. Nagel, E. Kinzel, J. Andrade, G. Prescher, Chem. Berl. 119 (1986) 3326;
(b) U. Nagel, B. Rieger, Organometallics 8 (1989) 1534;
(c) D. Lafont, D. Sinou, G. Descotes, J. Organomet. Chem. 169 (1979) 87;
(d) J. Bakos, B. Heil, L. Markó, J. Organomet. Chem. 253 (1983) 249;
(e) T.H. Johnson, G. Rangarajan, J. Org. Chem. 45 (1980) 62;
(f) I. Habuš, Z. Raza, V. Šunjić, Croat. Chim. Acta 61 (1988) 857;
(g) V. Šunjić, I. Habuš, G. Comisso, F. Moimas, Gazz. Chim. Ital. 119 (1989) 229;
(h) C. Li, B. B. Bernet, A. Vasella, E.A. Broger, A. Meili, Carbohydr. Res. (1991) 149;
(i) B.M. Choudary, M.R. Sarma, A.D. Prasad, N. Narender, Indian J. Chem. B 33 (1994) 152;
(j) S.R. Gilbertson, C.W.T. Chang, J. Org. Chem. 60 (1995) 6226;
(k) H. Brunner, R. Sievi, J. Organomet. Chem. 328 (1987) 71;
(l) H. Brunner, W. Pieronczyk, J. Chem. Res. (S) (1980) 76;
(m) M. Yamashita, K. Hiramatsu, M. Yamada, N. Suzuki, S. Inokawa, Bull. Chem. Soc. Japan 55 (1982) 2917;
(n) S. Saito, Y. Nakamura, Y. Morita, Chem. Pharm. Bull. 33 (1985) 5284;
(o) A. Iida, M. Yamashita, Bull. Chem. Soc. Japan 61 (1988) 2365;
(p) P. Lemaux, V. Massonneau, G. Simonneaux, J. Organomet. Chem. 284 (1985) 101.

[7] (a) O. Pàmies, G. Net, A. Ruiz, C. Claver, Eur. J. Inorg. Chem. (2000) 2011;
(b) M. Diéguez, O. Pàmies, A. Ruiz, S. Castillón, C. Claver, Tetrahedron: Asymmetry 11 (2000) 4701.

[8] Y.T. Wong, C. Yang, K.-C. Ying, G. Jia, Organometallics 21 (2002) 1782.

[9] W.R. Cullen, Y. Sugi, Tetrahedron Lett. 19 (1978) 1635.

[10] R. Jackson, D.J. Thompson, J. Organomet. Chem. 159 (1978) C29.

[11] R. Selke, React. Kinet. Catal. Lett. 10 (1979) 135.

[12] D. Sinou, G. Descotes, React. Kinet. Catal. Lett. 14 (1980) 463.

[13] (a) R. Selke, H. Pracejus, J. Mol. Catal. 37 (1986) 213;
(b) R. Selke, J. Prakt. Chem. 4 (1987) 717;
(c) R. Selke, J. Organomet. Chem. 370 (1989) 249;
(d) R. Selke, M. Scwarze, H. Baudish, I. Grassert, M. Michalik, G. Oehme, B. Costisella, J. Mol. Catal. 84 (1993) 223;
(e) R. Selke, M. Ohff, A. Riepe, Tetrahedron 52 (1996) 15079.

[14] (a) T.V. RajanBabu, T.A. Ayers, A.L. Casalnuovo, J. Am. Chem. Soc. 116 (1994) 4101;
(b) T.V. RajanBabu, T.A. Ayers, G.A. Halliday, K.K. You, J.C. Calabrese, J. Org. Chem. 62 (1997) 6012;
(c) T.A. Ayers, T.V. RajanBabu, US Patent 5510507 (1996).

[15] For related water soluble rhodium complexes, see:
Y.Y. Yan, T.V. RajanBabu, J. Org. Chem. 66 (2001) 3277.

[16] K. Yonehara, T. Hashizume, K. Ohe, S. Uemura, Bull. Chem. Soc. Japan 71 (1998) 1967.

[17] The water soluble deprotected-hydroxyl diphosphinite ligand **10** provides enantioselectivities up to 99%, see:
(a) K. Yonehara, K. Ohe, S. Uemura, J. Org. Chem. 64 (1999) 9381;
(b) K. Yonehara, T. Hashizume, K. Mori, K. Ohe, S. Uemura, J. Org. Chem. 64 (1999) 5593;
(c) S. Shin, T.V. RajanBabu, Org. Lett. 1 (1999) 1229.

[18] Y. Chen, X. Li, S. Tong, M.C.K. Choi, A.S.C. Chan, Tetrahedron Lett. 40 (1999) 957.

[19] S. Naili, I. Suisse, A. Mortreux, F. Agbossou, M.A. Ali, A. Karim, Tetrahedron Lett. 41 (2000) 2867.

[20] E. Guimet, M. Diéguez, A. Ruiz, C. Claver, Tetrahedron: Asymmetry 15 (2004) 2247.

[21] (a) M. Aghmiz, A. Aghmiz, Y. Díaz, A.M. Masdeu-Bultó, C. Claver, S. Castillón, J. Org. Chem. 69 (2004) 7502;
(b) M. Meseguer, H.-C. Militzer, S. Castillón, C. Claver, Y. Díaz, M. Aghmiz, E. Guiu, A. Masdeu, DE Patent 10241256 A1 (2004).

[22] E. Guiu, B. Muñoz, S. Castillón, C. Claver, Adv. Synth. Catal. 345 (2003) 169.

[23] R. Kadyrov, D. Heller, R. Selke, Tetrahedron: Asymmetry 9 (1999) 329.

[24] M.T. Reetz, T. Neugebauer, Angew. Chem. Int. Ed. 38 (1999) 179.

[25] (a) O. Pàmies, G. Net, A. Ruiz, C. Claver, Eur. J. Inorg. Chem. (2000) 1287;
(b) O. Pàmies, G. Net, A. Ruiz, C. Claver, Tetrahedron: Asymmetry 11 (2000) 1097;
(c) M. Diéguez, A. Ruiz, C. Claver, J. Org. Chem. 67 (2002) 3796.

[26] A. Gual, A.M.R. Axet, K. Philippot, B. Chaudret, B.A. Denicourt-Nowicki, A. Roucoux, S. Castillon, C. Claver, Chem. Commun. (2008) 2759.

[27] M.R. Axet, J. Benet-Buchholz, C. Claver, S. Castillón, Adv. Synth. Catal. 349 (2007) 1983.

[28] E. Engeldinger, D. Armspach, D. Matt, L. Toupet, M. Wesolek, C. R. Chemie (2002) 359.

[29] M.T. Reetz, G. Mehler, Angew. Chem. Int. Ed. 39 (2000) 3889.

[30] M.T. Reetz, L.J. Goosen, A. Meiswinkel, J. Paetzol, J.F. Jensen, Org. Lett. 5 (2003) 3099.

[31] (a) H. Huang, Z. Zheng, H. Luo, C. Bai, X. Hu, H. Chen, Org. Lett. 5 (2003) 4137;
(b) H. Huang, X. Liu, S. Chen, H. Chen, Z. Zheng, Tetrahedron: Asymmetry 15 (2004) 2011;
(c) H. Huang, Z. Zheng, H. Luo, C. Bai, X. Hu, H. Chen, J. Org. Chem. 69 (2004) 2335;
(d) H. Huang, X. Liu, H. Chen, Z. Zheng, Tetrahedron: Asymmetry 16 (2005) 693.

[32] M.T. Reetz, A. Gosberg, Tetrahedron: Asymmetry 10 (1999) 2129.

[33] K. Ohe, K. Morioka, K. Yonehara, S. Uemura, Tetrahedron: Asymmetry 13 (2002) 2155.

[34] (a) O. Pàmies, M. Diéguez, G. Net, A. Ruiz, C. Claver, Chem. Commun. (2000) 2383;
(b) O. Pàmies, M. Diéguez, G. Net, A. Ruiz, C. Claver, J. Org. Chem. 66 (2001) 8364.

[35] M. Diéguez, A. Ruiz, C. Claver, Chem. Commun. (2001) 2702.

[36] E. Guiu, M. Aghmiz, Y. Díaz, C. Claver, B. Meseguer, C. Militzer, S. Castillón, Eur. J. Org. Chem. (2006) 627.

[37] M. Diéguez, J. Mazuela, O. Pàmies, J.J. Verendel, P.G. Andersson, J. Am. Chem. Soc. 130 (2008) 7208.

[38] (a) N. Khiar, B. Suárez, M. Stiller, V. Valdivia, I. Fernández, Phosphorus Sulfur Silicon 180 (2005) 1253;
(b) N. Khiar, R. Navas, B. Suárez, E. Álvarez, I. Fernández, Org. Lett. 10 (2008) 3697.

[39] E. Guimet, M. Diéguez, A. Ruiz, C. Claver, Dalton Trans. (2005) 2557.

[40] (a) R.O. Duthaler, A. Hafner, M. Rjediker, Pure Appl. Chem. 62 (1990) 631;
(b) A. Hafner, R.O. Duthaler, R. Marti, G. Rihs, P. Rothe-Streit, F. Schwarzenbach, J. Am. Chem. Soc. 114 (1992) 2321.

[41] X.-R. Li, T.-P. Loh, Tetrahedron: Asymmetry 7 (1996) 1535.

[42] H.R. Appelt, J.B. Limberger, M. Weber, O.E.D. Rodrigues, J.S. Oliveira, D.S. Lüdtke, A.L. Braga, Tetrahedron Lett. 49 (2008) 4956.

[43] L. Pu, H.B. Yu, Chem. Rev. 101 (2001) 757.

[44] D.P.G. Emmerson, R. Villard, C. Mugnaini, A. Batsanov, J.A.K. Howard, W.P. Hems, R.P. Tooze, B.G. Davis, Org. Biomol. Chem. 1 (2003) 3826.
[45] D. Frantz, D.E. Fässler, E.M. Carreira, Acc. Chem. Res. 33 (2000) 373.
[46] D.P.G. Emmerson, W.P. Hems, B.G. Davies, Org. Lett. 8 (2006) 207.
[47] M. Irmak, M.M.K. Boysen, Adv. Synth. Catal. 350 (2008) 403.
[48] S. Woodward, Tetrahedron 58 (2002) 1017.
[49] (a) Y. Mata, M. Diéguez, O. Pàmies, S. Woodward, J. Org. Chem. 71 (2006) 8159; (b) E. Raluy, M. Diéguez, O. Pàmies, Tetrahedron: Asymmetry 20 (2009) 1575; (c) Y. Mata, M. Diéguez, O. Pàmies, S. Woodward, Inorg. Chim. Acta 361 (2008) 1381; (d) E. Raluy, M. Diéguez, O. Pàmies, Tetrahedron Lett. 50 (2009) 4495.
[50] (a) M. Kanai, N. Kato, E. Ichikawa, M. Shibasaki, Synlett (2005) 1491; (b) M. Shibasaki, M. Kanai, Org. Biomol. Chem. 5 (2007) 2027; (c) M. Shibasaki, M. Kanai, S. Matsunaga, N. Kumagai, Acc. Chem. Res. 42 (2009) 1117.
[51] Y. Hamashima, M. Kanai, M. Shibasaki, J. Am. Chem. Soc. 122 (2000) 7412.
[52] S. Masumoto, H. Usuda, M. Suzuki, M. Kanai, M. Shibasaki, J. Am. Chem. Soc. 125 (2003) 5634.
[53] T. Mita, I. Fujimori, R. Wada, J. Wen, M. Kanai, M. Shibasaki, J. Am. Chem. Soc. 127 (2005) 11252.
[54] T. Mita, K. Sasaki, M. Kanai, M. Shibasaki, J. Am. Chem. Soc. 127 (2005) 514.
[55] S.M. Ashraf, I. Berger, A.A. Nazarov, C.G. Hartinger, M.P. Koroteev, E.E. Nifant'ev, B.K. Keppler, Chem. Biodivers. 5 (2008) 1640.
[56] M. Spescha, Helv. Chim. Acta 76 (1993) 1832.
[57] M. Diéguez, A. Ruiz, C. Claver, Tetrahedron: Asymmetry 12 (2001) 2895.
[58] O. Pàmies, G. Net, A. Ruiz, C. Claver, S. Woodward, Tetrahedron: Asymmetry 11 (2000) 871.
[59] E. Guimet, M. Diéguez, A. Ruiz, C. Claver, Tetrahedron: Asymmetry 16 (2005) 2161.
[60] Y. Mata, M. Diéguez, O. Pàmies, S. Woodward, J. Organomet. Chem. 692 (2007) 4315.
[61] E. Raluy, O. Pàmies, M. Diéguez, S. Rosset, A. Alexakis, Tetrahedron: Asymmetry 20 (2009) 2167.
[62] E. Raluy, O. Pàmies, M. Diéguez, S. Rosset, A. Alexakis, Tetrahedron: Asymmetry 20 (2009) 1930.
[63] Y. Mata, M. Diéguez, O. Pàmies, K. Biswas, S. Woodward, Tetrahedron: Asymmetry 16 (2007) 1613.
[64] A. De Roma, F. Ruffo, S. Woodward, Chem. Commun. (2008) 5384.
[65] X. Pu, P. Li, F. Peng, X. Li, H. Zhang, Z. Shao, Eur. J. Org. Chem. (2009) 4622.
[66] S.M.W. Bennett, S.M. Brown, A. Cunningham, M.R. Dennis, J.P. Muxworthy, M.A. Oakley, S. Woodward, Tetrahedron 56 (2000) 2847.
[67] Z. Jászay, T.S. Pham, G. Németh, P. Bakó, I. Petneházy, L. Tőke, Synlett (2009) 1429.
[68] F. Tewes, A. Schlecker, K. Harms, F. Glorius, J. Organomet. Chem. 692 (2007) 4593.
[69] (a) J. Tsuji, Palladium Reagents and Catalysis. Innovations in Organic Synthesis, Wiley, New York, 1995; (b) B.M. Trost, D.L. van Vranken, Chem. Rev. 96 (1996) 395; (c) M. Johannsen, K.A. Jorgensen, Chem. Rev. 98 (1998) 1869; (d) B.M. Trost, M.L. Crawley, Chem. Rev. 103 (2003) 292; (e) Z. Lu, S. Ma, Angew. Chem. Int. Ed. 47 (2008) 258.
[70] (a) T. Hayashi, A. Yamamoto, T. Hagihara, Y. Ito, Tetrahedron Lett. 27 (1986) 191; (b) Recently this concept has also been use to explain the chiral induction by the Trost ligand, see: C.P. Butts, E. Filali, G.C. Lloyd-Jones, P.O. Norrby, D.A. Sale, Y. Schramm, J. Am. Chem. Soc. 131 (2009) 9945.
[71] See, for example: (a) B.M. Trost, R.C. Bunt, J. Am. Chem. Soc. 116 (1994) 4089; (b) B.M. Trost, A.C. Krueger, R.C. Bunt, J. Zambrano, J. Am. Chem. Soc. 118 (1996) 6520.
[72] See, for example: (a) G.J. Dawson, C.G. Frost, J.M.J. Williams, Tetrahedron Lett. 34 (1993) 3149; (b) P. von Matt, A. Pfaltz, Angew. Chem. Int. Ed. Engl. 32 (1993) 566; (c) J. Sprinz, G. Helmchen, Tetrahedron Lett. 34 (1993) 1769.
[73] M. Diéguez, O. Pàmies, Acc. Chem. Res. doi:10.1021/ar9002152.
[74] The flexibility that the biaryl moiety offers can be used to fine-tune the chiral pocket formed upon complexation. See, for example: (a) O. Pàmies, M. Diéguez, C. Claver, J. Am. Chem. Soc. 127 (2005) 3646; (b) Y. Mata, M. Diéguez, O. Pàmies, C. Claver, Adv. Synth. Catal. 347 (2005) 1943; (c) E. Raluy, O. Pàmies, M. Diéguez, J. Org. Chem. 72 (2007) 2842.
[75] See, for example: (a) G.P.F. van Strijdonck, M.D.K. Boele, P.C.J. Kamer, J.G. de Vries, P.W.N.M. van, Leeuwen, Eur. J. Inorg. Chem. (1999) 1073; (b) M. Diéguez, O. Pàmies, C. Claver, Adv. Synth. Catal. 347 (2005) 1257; (c) A. Balanta, I. Favier, E. Teuma, S. Castillón, C. Godard, A. Aghmiz, C. Claver, M. Gómez, Chem. Commun. (2008) 6197.
[76] R. Prétôt, A. Pfaltz, Angew. Chem. Int. Ed. 37 (1998) 323.
[77] B.M. Trost, Acc. Chem. Res. 29 (1996) 355.
[78] (a) M. Diéguez, S. Jansat, M. Gómez, A. Ruiz, G. Muller, C. Claver, Chem. Commun. (2001) 1132; (b) O. Pàmies, A. Ruiz, G. Net, C. Claver, H. Kalchhauser, M. Widhalm, Monatsch. Chem. 131 (2000) 1173.
[79] F. Ruffo, R. Del Lito, A. De Roma, A. D'Errico, S. Magnolia, Tetrahedron: Asymmetry 17 (2006) 2265.
[80] V. Benessere, A. De Roma, F. Ruffo, ChemSusChem 1 (2008) 425.
[81] R. Del Litto, V. Benessere, F. Ruffo, C. Moberg, Eur. J. Org. Chem. (2009) 1352.
[82] (a) N. Nomura, Y.C. Mermet-Bouvier, T.V. RajanBabu, Synlett (1996) 745; (b) D.S. Clyne, Y.C. Mermet-Bouvier, N. Nomura, T.V. RajanBabu, J. Org. Chem. 64 (1999) 7601.
[83] E. Guimet, M. Diéguez, A. Ruiz, C. Claver, Inorg. Chim. Acta 358 (2005) 3824.
[84] O. Pàmies, G.P.F. van Strijdonck, M. Diéguez, S. Deerenberg, G. Net, A. Ruiz, C. Claver, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Org. Chem. 66 (2001) 8867.
[85] (a) S. Jansat, M. Gómez, K. Philippot, G. Muller, E. Guiu, C. Claver, S. Castillón, B. Chaudret, J. Am. Chem. Soc. 126 (2004) 1592; (b) I. Favier, M. Gómez, G. Muller, M.R. Axet, S. Castillón, C. Claver, S. Jansat, B. Chaudret, K. Philippot, Adv. Synth. Catal. 349 (2007) 2459.
[86] M. Diéguez, O. Pàmies, C. Claver, J. Org. Chem. 70 (2005) 3363.
[87] See for instance: (a) B.L. Feringa, Acc. Chem. Res. 33 (2000) 346; (b) R.B.C. Jagt, P.Y. Toullec, D. Geerdink, J.G. de Vries, B.L. Feringa, A.J. Minnaard, Angew. Chem. Int. Ed. 45 (2006) 2789; (c) K. Tissot-Croset, D. Polet, A. Alexakis, Angew. Chem. Int. Ed. 43 (2004) 2426; (d) D. Polet, A. Alexakis, K. Tissot-Croset, C. Corminboeuf, K. Ditrich, Chem. Eur. J. 12 (2006) 3596; (e) M.D.K. Boele, P.C.J. Kamer, M. Lutz, A.L. Spek, J.G. de Vries, P.W.N.M. van Leeuwen, G.P.F. van Strijdonck, Chem. Eur. J. 10 (2004) 6232; (f) O. Pàmies, M. Diéguez, Chem. Eur. J. 14 (2008) 944; (g) O. Pàmies, M. Diéguez, C. Claver, Adv. Synth. Catal. 349 (2007) 836; (h) K. Biswas, O. Prieto, P.J. Goldsmith, S. Woodward, Angew. Chem. Int. Ed. 44 (2005) 2232; (i) A. Alejakis, C. Benhaim, S. Rosset, M. Humam, J. Am. Chem. Soc. 124 (2002) 5262.
[88] (a) A.M. Masdeu-Bultó, M. Diéguez, E. Martin, M. Gómez, Coord. Chem. Rev. 242 (2003) 159; (b) E. Martin, M. Diéguez, C. R. Chemie 10 (2007) 188; (c) F. Fernández, M. Gomez, S. Jansat, G. Muller, E. Martín, L. Flores-Santos, P.X. Garcia, A. Acosta, A. Aghmiz, M. Gimenez-Pedros, A.M. Masdeu-Bultó, M. Diéguez, C. Claver, M.A. Maestro, Organometallics 24 (2005) 3946; (d) S. Jansat, M. Gomez, G. Muller, M. Diéguez, A. Aghmiz, C. Claver, A.M. Masdeu-Bultó, L. Flores-Santos, E. Martín, M.A. Maestro, J. Mahía, Tetrahedron: Asymmetry 12 (2001) 1469.
[89] (a) N. Khiar, C.S. Araújo, E. Alvarez, I. Fernández, Tetrahedron Lett. 44 (2003) 3401; (b) N. Khiar, C.S. Araújo, B. Suárez, I. Fernández, Eur. J. Org. Chem. (2006) 1685.
[90] (a) E. Raluy, C. Claver, O. Pàmies, M. Diéguez, Org. Lett. 9 (2007) 49; (b) E. Raluy, O. Pàmies, M. Diéguez, Adv. Synth. Catal. 351 (2009) 1648.
[91] Y. Mata, M. Dièguez, O. Pàmies, C. Claver, Tetrahedron: Asymmetry 17 (2006) 3282.
[92] B. Gläser, H. Kunz, Synlett (1998) 53.
[93] (a) K. Yonehara, T. Hashizume, K. Mori, K. Ohe, S. Uemura, Chem. Commun. (1999) 415; (b) K. Yonehara, T. Hashizume, K. Mori, K. Ohe, S. Uemura, J. Org. Chem. 64 (1999) 9374.
[94] For related water soluble ligands, see: T. Hashizume, K. Yonehara, K. Ohe, S. Uemura, J. Org. Chem. 65 (2000) 5197.
[95] (a) Y. Mata, M. Diéguez, O. Pàmies, C. Claver, Adv. Synth. Catal. 347 (2005) 1947; (b) Y. Mata, M. Diéguez, O. Pàmies, Adv. Synth. Catal. 351 (2009) 3217.
[96] M. Diéguez, O. Pàmies, Y. Mata, E. Teuma, F. Ribaudo, P.W.N.M. van Leeuwen, Adv. Synth. Catal. 350 (2008) 2583.
[97] (a) C. Borriello, M.E. Cucciolito, A. Panunzi, F. Ruffo, Inorg. Chim. Acta 353 (2003) 238; (b) H. Brunner, M. Schönherr, M. Zabel, Tetrahedron: Asymmetry 14 (2003) 1115; (c) S.A. Johannensen, K. Glegola, D. Sinou, E. Framery, T. Skrydstrup, Tetrahedron Lett. 48 (2007) 3569; (d) K. Glegola, S.A. Johannensen, L. Thim, C. Goux-Henry, T. Skrydstrup, E. Framery, Tetrahedron Lett. 49 (2008) 6635.
[98] (a) A. Albinati, P.S. Pregosin, K. Wick, Organometallics 15 (1996) 2419; (b) P. Barbaro, A. Currao, J. Herrmann, R. Nesper, P.S. Pregosin, R. Salzmann, Organometallics 15 (1996) 1879.
[99] (a) N. Khiar, B. Suàrez, I. Fernández, Inorg. Chim. Acta 359 (2006) 3048; (b) N. Khiar, R. Navas, E. Álvarez, I. Fernánadez, ARKIVOC (2008) 211.
[100] H. Nakano, J. Yokohama, Y. Okuyama, R. Fujita, H. Hongo, Tetrahedron: Asymmetry 14 (2003) 2361.
[101] (a) E. Guimet, M. Diéguez, A. Ruiz, C. Claver, Tetrahedron: Asymmetry 16 (2005) 959; (b) M. Diéguez, O. Pàmies, C. Claver, J. Organomet. Chem. 691 (2006) 2257.
[102] N. Khiar, B. Suárez, V. Valdivia, I. Fernández, Synlett (2005) 2963.
[103] (a) M. Tollabi, E. Framery, C. Goux-Henry, D. Sinou, Tetrahedron: Asymmetry 14 (2003) 3329; (b) A. Konovets, K. Glegola, A. Penciu, E. Framery, P. Jubault, C. Goux-Henry, K.M. Pietrusiewicz, J.C. Quirion, D. Sinou, Tetrahedron: Asymmetry 16 (2005) 3183; (c) K. Glegola, E. Framery, C. Goux-Henry, K.M. Pietrusiewicz, D. Sinou, Tetrahedron 63 (2007) 7133; (d) T. Bauer, A. Bartoszewicz, Polish J. Chem. 81 (2007) 2115.
[104] K. Boog-Wick, P.S. Pregosin, G. Trabesinger, Organometallics 17 (1998) 3254.

[105] For reviews see:
(a) L.T. Tietze, H. Ila, H.P. Bell, Chem. Rev. 104 (2004) 3453;
(b) L.X. Dai, T. Tu, S.L. You, W.P. Deng, X.L. Hou, Acc. Chem. Res. 36 (2003) 659;
(c) C. Bolm, J.P. Hildebrand, K. Muñiz, N. Hermanns, Angew. Chem. Int. Ed. 44 (2001) 3284;
(d) O. Loiseleur, M. Hayashi, M. Keenan, N. Schemees, A. Pfaltz, J. Organomet. Chem. 576 (1999) 16;
(e) M. Beller, T.H. Riermeier, G. Stark, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, Wiley-VCH, Weinheim, 1998;
(f) A.B. Dounay, L.E. Overman, Chem. Rev. 103 (2003) 2945.
[106] See for instance:
(a) O. Loiseleur, P. Meier, A. Pfaltz, Angew. Chem. Int. Ed. Engl. 35 (1996) 200;
(b) O. Loiseleur, M. Hayashi, N. Schmees, A. Pfaltz, Synthesis (1997) 1338;
(c) T. Tu, X.L. Hou, L.X. Dai, Org. Lett. 5 (2003) 3651;
(d) S.R. Gilbertson, D. Xie, Z. Fu, J. Org. Chem. 66 (2001) 7240;
(e) S.R. Gilbertson, Z. Fu, Org. Lett. 3 (2001) 161;
(f) T. Tu, W.P. Deng, X.L. Hou, L.X. Dai, X.C. Dong, Chem. Eur. J. 9 (2003) 3073;
(g) S.R. Gilbertson, D.G. Genov, A.L. Rheingold, Org. Lett. 2 (2000) 2885;
(h) Y. Hashimoto, Y. Horie, M. Hayashi, K. Saigo, Tetrahedron: Asymmetry 11 (2000) 2205;
(i) X.L. Hou, D.X. Dong, K. Yuan, Tetrahedron: Asymmetry 15 (2004) 2189;
(j) D. Liu, Q. Dai, X. Zhang, Tetrahedron 61 (2005) 6460;
(k) W.Q. Wu, Q. Peng, D.X. Dong, X.L. Hou, Y.D. Wu, J. Am. Chem. Soc. 130 (2008) 9717;
(l) M. Rubina, W.M. Sherrill, M. Rubin, Organometallics 27 (2008) 6393;
(m) K. Yonehara, K. Mori, T. Hashizume, K.G. Chung, K. Ohe, S. Uemura, J. Organomet. Chem. 603 (2000) 40;
(n) W.J. Drury III, N. Zimmermann, M. Keenan, M. Hayashi, S. Kaiser, R. Goddard, A. Pfaltz, Angew. Chem. Int. Ed. 43 (2004) 70;
(o) S.T. Henriksen, P.O. Norrby, P. Kaukoranta, P.G. Andersson, J. Am. Chem. Soc. 130 (2008) 10414;
(p) Y. Mata, O. Pàmies, M. Diéguez, Org. Lett. 7 (2005) 5597;
(q) Y. Mata, O. Pàmies, M. Diéguez, Chem. Eur. J. 13 (2007) 3296;
(r) J. Mazuela, O. Pàmies, M. Diéguez, Chem. Eur. J. doi:10.1002/chem.200902777.
[107] See for example:
(a) C. Claver, M. Diéguez, O. Pàmies, S. Castillón, in: M. Beller (Ed.), Topics in Organometallic Chemistry, Springer, Berlin, 2006 (Chapter 2, 35);
(b) C. Claver, C. Godard, A. Ruiz, O. Pàmies, M. Diéguez, in: L. Kollár (Ed.), Modern Carbonylation Methods, Wiley-VCH, Weinheim, 2008 (Chapter 3);
(c) K. Nozaki, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Springer, Berlin, 1999 (Chapter 11, 382).
[108] See for example:
(a) M. Diéguez, O. Pàmies, C. Claver, Tetrahedron: Asymmetry 15 (2004) 2113;
(b) B. Breit, Top. Curr. Chem. 279 (2007) 139;
(c) J. Klosin, C.R. Landis, Acc. Chem. Res. 40 (2007) 1251;
(d) P.W.N.M. van Leeuwen, C. Claver (Eds.), Rhodium Catalysed Hydroformylation, Kluwer Academic Press, Dordrecht, 2000.
[109] See for example:
(a) A.T. Axtell, C.J. Cobley, J. Klosin, G.T. Whiteker, A. Zanotti-Gerosa, K.A. Abboud, Angew. Chem. Int. Ed. 44 (2005) 5834;
(b) J. Huang, E. Bunel, A. Allgeier, J. Tedrow, T. Storz, J. Preston, T. Correll, D. Manley, T. Soukup, R. Jensen, R. Syed, G. Moniz, R. Larsen, M. Martinelli, P.J. Reider, Tetrahedon Lett. 46 (2005) 7831.
[110] See for instance:
(a) T.P. Clark, C.R. Landis, S.L. Freed, J. Klosin, K.A. Abboud, J. Am. Chem. Soc. 127 (2005) 5040;
(b) P.J. Thomas, A.T. Axtell, J. Klosin, W. Peng, C.L. Rand, T.P. Clark, C.R. Landis, K.A. Abboud, Org. Lett. 9 (2007) 2665;
(c) S. Breeden, D.J. Cole-Hamilton, D.F. Foster, G.J. Schwarz, M. Wills, Angew. Chem. Int. Ed. 39 (2000) 4106;
(d) X. Peng, Z. Wang, C. Xia, K. Ding, Tetrahedron Lett. 49 (2008) 4862.
[111] Y. Yan, X. Zhang, J. Am. Chem. Soc. 128 (2006) 7198.
[112] (a) S. Liu, X. Li, A. Wang, Catal. Today 63 (2000) 531;
(b) M. Diéguez, O. Pàmies, G. Net, A. Ruiz, C. Claver, Tetrahedron: Asymmetry 12 (2001) 651.
[113] (a) T.V. RajanBabu, T.A. Ayers, Tetrahedron Lett. 35 (1994) 4295;
(b) T. Ayers, T.V. RajanBabu, U.S. Patent 5475146 (1995);
(c) E. Guimet, J. Parada, M. Dieguez, A. Ruiz, C. Claver, Appl. Catal. A: Gen. 282 (2005) 215.
[114] (a) G.J.H. Buisman, M.E. Martin, E.J. Vos, A. Klootwijk, P.C.J. Kamer, P.W.N.M. van Leeuwen, Tetrahedron: Asymmetry 8 (1995) 719;
(b) M. Diéguez, O. Pàmies, A. Ruiz, S. Castillón, C. Claver, Chem. Commun. (2000) 1607;
(c) M. Diéguez, O. Pàmies, A. Ruiz, S. Castillón, C. Claver, Chem. Eur. J. 7 (2001) 3086;
(d) M. Diéguez, O. Pàmies, A. Ruiz, C. Claver, New J. Chem. 26 (2002) 827.
[115] (a) M. Diéguez, O. Pàmies, C. Claver, Chem. Commun. (2005) 1221;
(b) J. Mazuela, M. Coll, O. Pàmies, M. Diéguez, J. Org. Chem. 74 (2009) 5440.
[116] A. Gual, C. Godard, C. Claver, S. Castillón, Eur. J. Org. Chem. (2009) 1191.
[117] (a) O. Pàmies, G. Net, A. Ruiz, C. Claver, Tetrahedron: Asymmetry 12 (2001) 3441;
(b) M. Diéguez, A. Ruiz, C. Claver, Tetrahedron: Asymmetry 12 (2001) 2827;
(c) O. Pàmies, M. Diéguez, G. Net, A. Ruiz, C. Claver, Organometallics 19 (2000) 1488;
(d) A. Kless, J. Holz, D. Heller, R. Kadirov, R. Selke, C. Fischer, A. Börner, Tetrahedron: Asymmetry 7 (1996) 33.
[118] S. Yan, D. Klemm, Tetrahedron 58 (2002) 10065.
[119] J. Zhao, Y. Zhang, F. Han, S. Zhao, Carbohydr. Res. 344 (2009) 61.
[120] C. Borriello, R.D. Litto, A. Panunzi, F. Ruffo, Tetrahedron: Asymmetry 15 (2004) 681.
[121] J. Fridgen, W.A. Herrmann, G. Eickerling, A.M. Santos, F.E. Kühn, J. Organomet. Chem. 689 (2004) 2752.
[122] (a) I. Lippolda, J. Becherb, D. Klemm, W. Plass, J. Mol. Catal. (A) 299 (2009) 12;
(b) M.E. Cucciolito, R. Del Litto, G. Roviello, F. Ruffo, J. Mol. Catal. (A) 236 (2005) 176.
[123] F. Han, J. Zhao, Y. Zhang, W. Wang, Y. Zuo, J. An, Carbohydr. Res. 343 (2008) 1407.
[124] A. Assalit, T. Billard, S. Chambert, B.R. Langlois, Y. Queneau, D. Coe, Tetrahedron: Asymmetry 20 (2009) 593.
[125] (a) M. Irmak, A. Groschner, M.M.K. Boysen, Chem. Commun. (2007) 177;
(b) T. Minuth, M. Irmak, A. Groschner, T. Lehnert, M.M.K. Boysen, Eur. J. Org. Chem. (2009) 997;
(c) M. Irmak, T. Lehnert, M.M.K. Boysen, Tetrahedron Lett. 48 (2007) 7890;
(d) T. Minuth, M.M.K. Boysen, Org. Lett. 11 (2009) 4212.
[126] A.L. Casalnuovo, T.V. RajanBabu, T.A. Ayers, T.H. Warren, J. Am. Chem. Soc. 116 (1994) 9869.
[127] H. Park, R. Kumareswaran, T.V. RajanBabu, Tetrahedron 61 (2005) 6352.
[128] K.P.R. Kartha, Tetrahedron Lett. 27 (1986) 3415.
[129] A.I. Vogel, Vogel's Textbook of Practical Organic Chemistry, 5th ed., Longman, New York, 1994.
[130] R.E. Arrick, D.C. Baker, D. Horton, Carbohydr. Res. 26 (1973) 441.
[131] (a) O.T. Schmidt, in: R.L. Whistler, M.L. Wolfrom (Eds.), Methods in Carbohydrate Chemistry, vol. 2, Academic Press, New York, 1963;
(b) G.N. Austin, P.D. Baird, G.W.J. Fleet, J.M. Peach, P.W. Smith, D.J. Watkin, Tetrahedron 43 (1987) 3095.
[132] G.J.L. Bernardes, J.P. Marston, A.S. Batsanov, J.A.K. Howard, B.G. Davis, Chem. Commun. (2007) 3145.
[133] P. Czechura, R.Y. Tam, E. Dimitrijevic, A. Murphy, R.N. Ben, J. Am. Chem. Soc. 130 (2008) 2928.
[134] P.R. Patil, K.P.R. Kartha Jr., Carbohydr. Chem. 27 (2008) 411.
[135] E.J. Cocinero, D.P. Gamblin, B.G. Davis, J.P. Simons, J. Am. Chem. Soc. 131 (2009) 11117.
[136] K.C. Nicolaou, J.L. Randall, G.T. Furst, J. Am. Chem. Soc. 107 (1985) 5556.
[137] Y. Tu, M. Frohn, Z.-X. Wang, Y. Shi, Org. Synth. 80 (2003) 1.
[138] R.F. Brady Jr., Carbohydr. Res. 15 (1970) 35.
[139] C.R. Schmid, J.D. Bryant, M. Dowlatzedah, J.L. Phillips, D.E. Prather, R.D. Schantz, N.L. Sear, C.S. Vianco, J. Org. Chem. 56 (1991) 4056.
[140] (a) H. Liang, T.B. Grindley Jr., Carbohydr. Res. 23 (2004) 71;
(b) D. Horton, H. Mayer Jr., R. Montgomery, Biochem. Prep. 11 (1966) 1.
[141] W. Roth, W. Pigman, J. Am. Chem. Soc. 82 (1960) 4608.
[142] (a) D. Horton, K.D. Philips, Methods Carbohydr. Chem. 7 (1976) 68;
(b) D.A. Otero, R. Simpson, Carbohydr. Res. 128 (1984) 79;
(c) S. Claustre, F. Bringaud, L. Azéma, R. Baron, J. Périé, M. Willson, Carbohydr. Res. 315 (1999) 339.
[143] D. Wahler, O. Boujard, F. Lefèvrea, J.-L. Reymond, Tetrahedron 60 (2004) 703.
[144] K. C: Nicolaou, J. Li, G. Zenke, Helv. Chim. Acta 83 (2000) 1977.