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Chiral single-atom-bridged diphosphorus ligands: synthesis, complexation and catalysis†

Javier Eusamio [a,b] and Arnald Grabulosa *[a,b]

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The synthesis, complexation and main catalytic applications in enantioselective homogeneous catalysis of enantiopure single-atom-bridged diphosphorus ligands ($(R^1R^2)P–X–P(R^3R^4)$; X = CR_2, NR, O) is reviewed, covering the literature up to the beginning of 2025. The information is organised by ligand type, with unsubstituted methylene-bridged (–CH_2–) and substituted amino-bridged (–NR–) diphosphorus ligands being by far the most common type of ligands. The perspective review is completed by the analysis of all reported crystal structures of bidentate monometallic complexes with the ligands. The bite angles, metal–phosphorus distances and buried volumes (V_{bur}) are given in the ESI.†

Introduction

The development of new chiral ligands for enantioselective homogeneous catalysis[1] has been tremendous during the last four decades and shows no signs of diminution. Despite the plethora of coordination motifs currently in use, diphosphorus ligands[2] constitute the most important class of ligands for many reactions. Hundreds, if not thousands of chiral diphosphorus ligands have been described in the literature, many of them with complicated, yet captivating structures. However, this beauty comes with a price as they are obtained by lengthy, multistep syntheses.

One of the key parameters of diphosphorus ligands is the bite angle,[3] whose structural and catalytic effects have been studied and exploited to a great effect. Another parameter is the bulkiness of the ligands, and recently the buried volume has emerged as a way to parametrize[4,5] the steric hindrance of a ligand (Fig. 1A).[6–8]

The simplest bridge is a single atom, and this is incarnated by the ligand 1,2-bis(diphenylphosphino)methane (dppm), a ligand synthesised as early as 1959 by Issleib and Müller[9] and used to prepare countless coordination and organometallic compounds. This simplicity can turn into advantage, because it is instructive to recall that some of the best ligands in

[a]*Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica, Universitat de Barcelona, Martí i Franquès, 1-11, E-08028 Barcelona, Spain. E-mail: arnald.grabulosa@ub.edu*
[b]*Institut de Nanociència i Nanotecnologia (IN2UB), Universitat de Barcelona, E-08028 Barcelona, Spain*

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Javier Eusamio

Javier Eusamio obtained his BSc in Chemistry at the University of Barcelona (UB) in 2020 and a MSc in Applied Materials Science in 2021. He is currently finishing his PhD in the Inorganic and Organic Chemistry Department of UB, under the supervision of Dr Arnald Grabulosa. His research interests focus on the synthesis of diphosphorus ligands and their coordination to late transition metals for homogeneous catalysis. In parallel, he pursues a MSc in Computational and Mathematical Engineering.

Arnald Grabulosa

Arnald Grabulosa obtained his PhD in Inorganic Chemistry from the University of Barcelona (UB) in 2005 with Prof. Muller. After postdoctoral periods with Profs Gros (Nancy, France), Kamer and Clarke (St Andrews, UK), in 2017 he earned an Assistant Professorship at the Inorganic and Organic Chemistry Department of UB. His research focuses on coordination and organometallic chemistry with novel phosphorus ligands for catalysis and other applications.

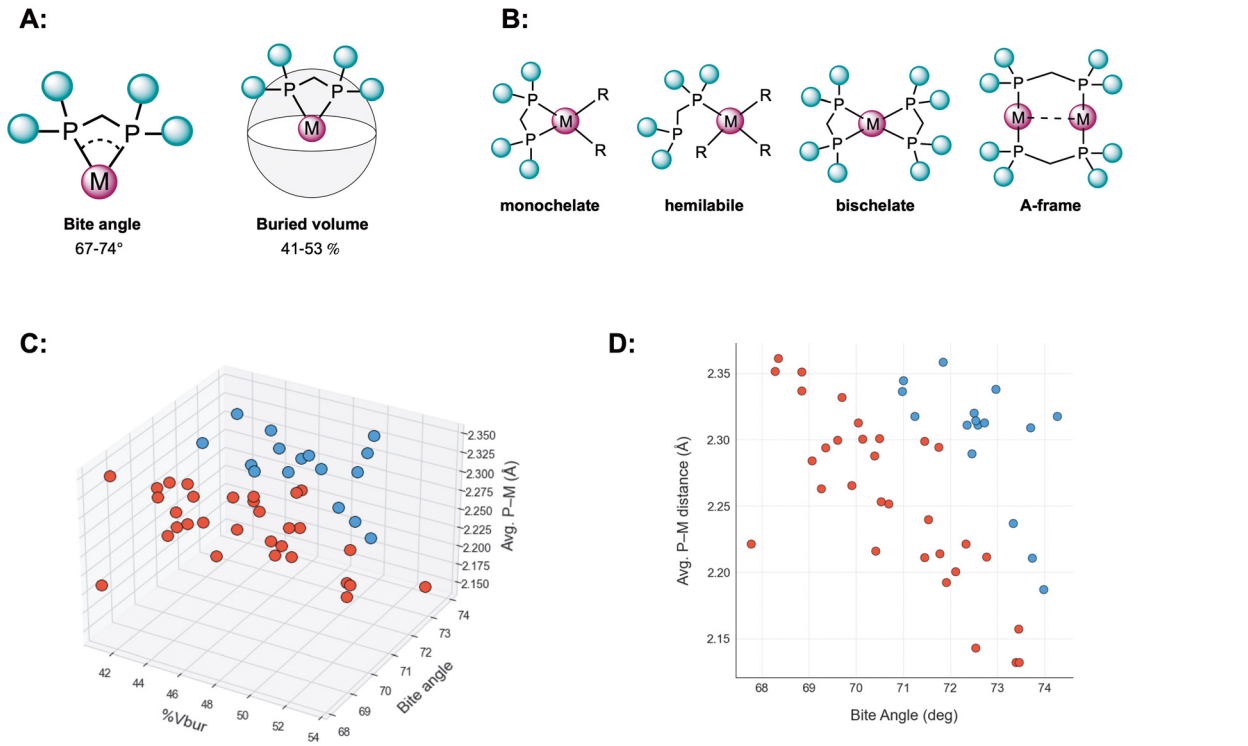


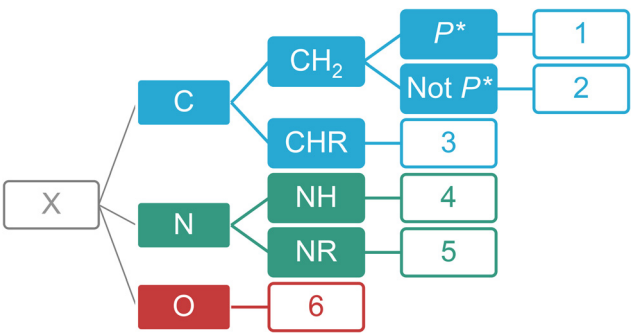
Fig. 1 (A) Representation of the bite angle and buried volume, and the value ranges of complexes with chiral PXP ligands coordinated in bidentate fashion. (B) Typical coordination motifs in complexes with PXP ligands. (C) 3D scatter plot of the buried volumes (%V_{bur}), bite angles, and average P–M distances of the 47 reported crystal structures of monometallic complexes coordinated to chiral single-atom-bridged diphosphanes in a bidentate way. *N*-bridged diphosphanes (PNP) are shown in red, while *C*-bridged diphosphanes (PCP) are represented in blue. (D) Slice of plot C showing only the average P–M distance *vs.* the bite angle.

enantioselective hydrogenation[10] are methylene-bridged chiral diphosphanes, some of them with a single stereogenic centre. In addition, the coordination of single-atom-bridged diphosphorus ligands is far from simple because other coordination modes apart from the expected bidentate coordination forming four-membered chelates are known (Fig. 1B).[11,12]

In 2017 S. Mansell published a fascinating perspective on the catalytic applications of diphosphorus ligands with single-atom linkers.[11] Inspired by this publication and our own work in the field, we herewith review the *enantiopure* single-atom-bridged diphosphorus ligands described so far, with a general formula ((R^1R^2)P–X–P(R^3R^4); X = CR_2, NR, O), abbreviated as PXP. Although they constitute a relatively small subset of ligands, some of them excel in enantioselective catalysis, particularly in hydrogenation.

There are many ways to classify diphosphorus ligands. In the case of single-atom-bridge ligands (PXP), a convenient way is depicted in Scheme 1.

The ligands are firstly classified by the bridging atom between the phosphorus atoms. In the case of the chiral ligands treated in this review, only carbon, nitrogen and oxygen examples have been described so far. Then the carbon- and nitrogen-based ligands are subdivided according to the substitution or not of the atom in the bridge. The unsubstituted, methylene-bridged ligands can be then subdivided into



Scheme 1 Classification of the PXP ligands used in this perspective article.

P-stereogenic (denoted as P*, type 1) or not (type 2). There are only a few PCP ligands with a substituted methylene bridge, which form group 3. The same is true for PNP ligands with an unsubstituted nitrogen bridge (NH, group 4) but there are many ligands with a substituted nitrogen bridge, which constitute group 5. Finally, there is the small subset of ligands with an oxygen bridge (POP), which constitutes group 6.

This classification according to the bridging atom has been conceived as a way to systematise the different ligands present in this review, but it can be observed in Fig. 1(C and D) that

the bridging atom does indeed greatly affect the geometry of the ligand and, consequently, its coordination and its behaviour in catalysis.

Fig. 1C is a 3D scatter plot of all the crystal structures of chiral PXP diphosphorus ligands. Only monometallic bidentate complexes, with a bidentate coordination of the ligand have been considered. Interestingly, the difference between PNP and PCP ligands, represented as red and blue points respectively, can be readily observed, as the two types of ligands appear in two differentiated clusters. This can be observed even better in Fig. 1D, when a 2D slice of the previous plot is represented. As expected, the smaller the P–M distance the bigger the bite angle, although this trend is clearer with *N*-bridged ligands. It can also be observed that there is a noticeable correlation between buried volume and bite angle, with the bulkier ligands generally having wider bite angles (ESI, Fig. S3†). Interestingly, **L73** (Fig. 3) presents the smallest bite angle and second smallest buried volume at a sphere radius of 3.5 Å (Table S1†), even though the diphosphane contains two apparently bulky BINAP moieties (Fig. 3). On the other hand, the bulkier diphosphane corresponds to MaxPHOS (**L54**, Fig. 3), of which multiple crystal structures have been analyzed. As expected, when coordinated to nickel (II) center, **L54** is significantly bulkier and has a smaller P–M distance due to the smaller size of the nickel cation. In general, it appears that complexes with PNP ligands appear across a wider range of values than those with PCP ligands (ESI, Fig. S1–S4†). However, this could be because there are more structures for the former type of ligands, and that the metal centers of the complexes are also more varied.

All the ligands described so far are collected in Fig. 2 (PCP ligands) and Fig. 3 (PNP ligands), with the number used to refer to them in this perspective.

A quick glance at Fig. 2 and 3 shows that most of the ligands are either methylene-bridged (types 1 and 2) or with a substituted nitrogen bridge (type 5). It can be observed that many of the ligands contain a *P*-stereogenic group, especially in the more recently reported ligands.[13,14] Apparently, it is an excellent motif in the four-membered chelated structures formed in the coordination of single-atom bridged ligands.

The reader may wonder why there are so few examples of oxygen-bridged ligands or whether other bridges, for example with sulphur, are possible. The answer is that oxygen (POP) and sulphur (PSP) ligands undergo a phosphorotropic equilibrium between the bis(phosphorus(III)) tautomer (PXP) and the phosphorus(II)–(III) tautomer (PPX, Scheme 2).[15]

This equilibrium is reminiscent to that present between secondary phosphane oxides (SPOs) and phosphinous acids[16] and depends on the bridging atom and the substituents present on the phosphorus atom. In the case of nitrogen, the equilibrium almost always lies towards the PNP side, and this has been exploited to prepare a plethora of ligands. In contrast, for oxygen and sulphur, it usually lies towards the PPX side, explaining their rarity. Like in the case of SPOs, however, it is possible to stabilise the PXP tautomer by coordination and so they should not be discarded for catalysis,[16–19] although to the best of our knowledge this has not been used in enantioselective catalysis.

The review summarises the chemistry involved in the preparation and complexation of the PXP ligands and their main applications in enantioselective catalysis. In addition, the crystal structures of all the coordination and organometallic complexes described so far with the ligands have been analysed to extract the bite angles, phosphorus-metal distances and buried volumes (V_{bur}),[7] given in the ESI.† The review covers the primary literature up to the beginning of 2025.

C-bridged diphosphorus ligands (PCP)

There are, to our knowledge, 52 examples of enantiopure *C*-bridged diphosphorus ligands described in the literature (**L1–L52**, Fig. 2). Interestingly, most of them contain an unsubstituted methylene bridge (**L1–L41**), with only 11 examples in which the bridge is substituted (**L42–L52**, Fig. 2).[20–22] In all cases, one of the phosphorus is part of a cycle, and there are no examples in the literature with acyclic substituted or disubstituted carbon bridges.

We have firstly divided this section into methylene bridged ligands and ligands with a substituted bridge, with the former subsection being the one with the most ligands. For this reason and taking into account that most of the PCP ligands are *P*-stereogenic, the methylene-bridged diphosphanes have been further divided into alkyl-substituted *P*-stereogenic, aryl-substituted *P*-stereogenic, and non-*P*-stereogenic. This layout appears to be the most natural, since most of the alkyl-substituted *P*-stereogenic ligands show common synthetic strategies, and the same applies with their aryl-substituted counterparts. Furthermore, this classification provides a good overview of some of the most relevant synthetic methodologies for obtaining *P*-stereogenic ligands, which could be of interest since the control of the configuration of a stereogenic phosphorus is a challenging topic.[13,14]

Methylene-bridged *P*-stereogenic diphosphorus ligands

Alkyl-substituted *P*-stereogenic diphosphanes. In 1995, Evans and coworkers reported a method for the enantioselective deprotonation (desymmetrisation) of phosphane–boranes and phosphane sulphides using *s*-BuLi as a base and (−)-sparteine as a chiral auxiliary.[23] However, they only explored this reactivity with aryl substituted monophosphanes to form ethylene-bridged diphosphanes. Shortly after, in 1998, Imamoto and coworkers applied this same methodology to obtain fully alkyl-substituted monophosphanes, which were used for the synthesis of the so-called BisP* ligands,[24] which also have an ethylene bridge.

Immediately after, Imamoto and coworkers applied the previously reported methodology for the synthesis of fully-alkyl methylene-bridged diphosphanes and developed the well-known MiniPHOS ligands (**L1–L7**), which are nowadays still regarded among the best ligands for enantioselective hydrogenation of functionalized olefins.[25]

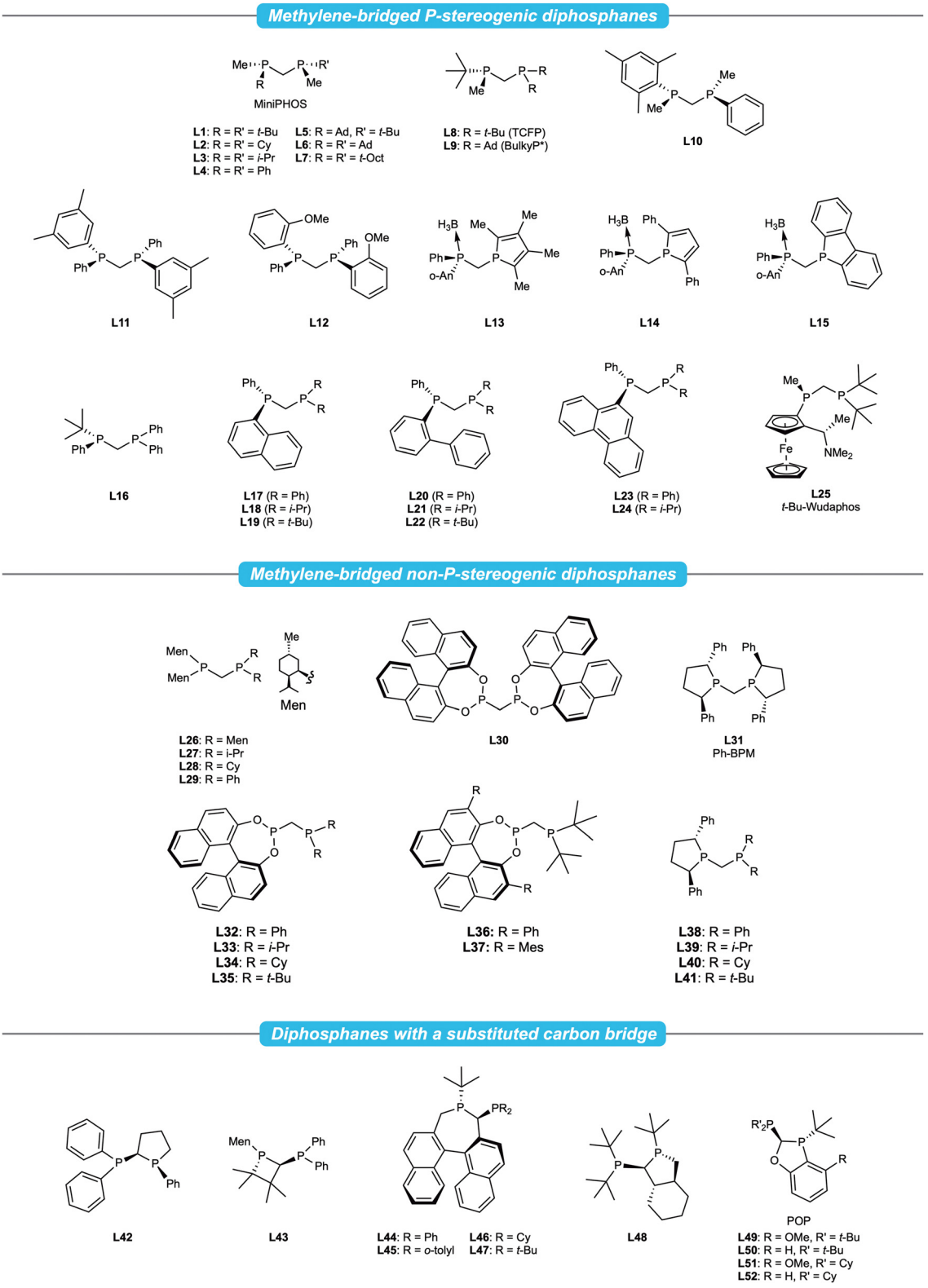


Fig. 2 *C*-bridged diphosphorus ligands (PCP).

Their synthesis (Scheme 3) started with the preparation of alkyldimethylphosphane–boranes from PCl_3 in two simple steps, followed by the stereoselective deprotonation of one of the methyl groups through the Evans method (enantioselective deprotonation), followed by reaction of the carbanion with one equivalent alkyldichlorophosphane followed by addition of

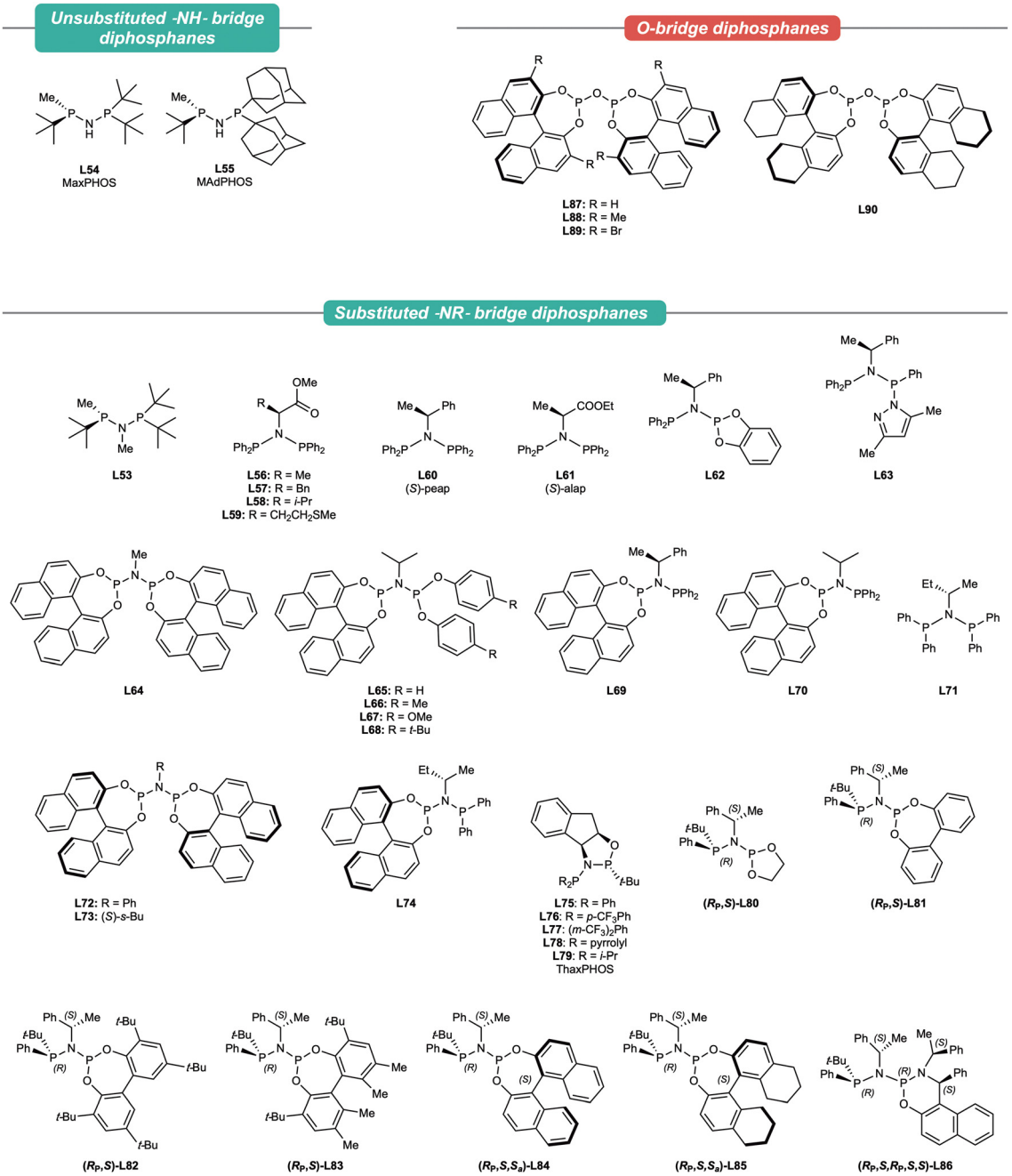
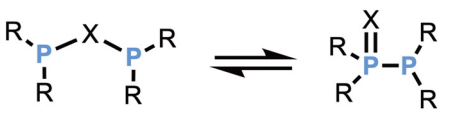


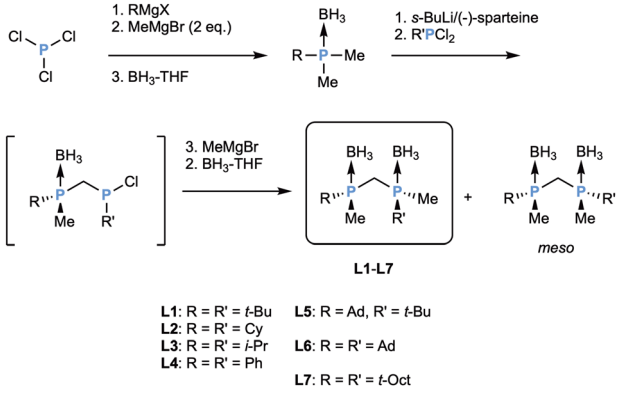
Fig. 3 *N*- and *O*-bridged chiral diphosphorus ligands (PNP and POP, respectively).



Scheme 2 Phosphorotropic tautomerism between PXP (left) and PPX (right).

methylmagnesium bromide and boronation to protect the newly formed phosphane moiety. Since the addition of the second phosphane is not stereoselective (a *P*-stereogenic atom is formed), this reaction yielded two diastereomers, the optically active one, and the *meso* form. Luckily, in most cases they could be separated through recrystallization to obtain the pure protected ligands (Scheme 3), which could then be deboronated with triflic acid for their complexation. The obtained free diphosphanes were air-sensitive but configurationally stable at room temperature.

Among the four original MiniPHOS (**L1–L4**) ligands,[25] it appeared that *t*-Bu-MiniPHOS (**L1**) was the one that afforded the best results in the initial enantioselective catalytic reactions studied (Michael additions and hydrogenation, Fig. 5).



Scheme 3 Synthesis of MiniPHOS ligands (**L1–L7**).

Shortly after,[26] they synthesized two new MiniPHOS (**L5** and **L6**) ligands, this time bearing 1-adamantyl substituents. Interestingly, ligand **L5** is the first (and one of the very few) reported C_1-symmetric, methylene-bridged *P*-stereogenic ligands. A few years later,[27] a new ligand **L7**, bearing *t*-octyl substituents, was also developed by a different procedure, using an optically pure secondary methylphosphane–borane as starting material.[27]

Surprisingly, when the coordination of **L1** to rhodium(I)-diene moieties was explored, it was observed that, due to their small bite angle, a bischelated complex bis-**C1** (Fig. 4) tends to form instead of the expected monochelated complex (**C1**), regardless of stoichiometry. This is a behaviour that has also been observed with other chiral PXP ligands.[28–30]

Interestingly, the formation of this bischelated complex could be easily avoided by using $[Rh(cod)_2]SbF_6$ as a metal precursor instead of $[Rh(nbd)_2]SbF_6$.[31]

In the case of **L1**, the mechanism of the catalytic activity of the bischelated complex in enantioselective hydrogenation was thoroughly studied by Imamoto and Gridnev.[27,32–34] A hemilabile behaviour was proposed to justify the coordination of the substrate to the octahedral dehydrogenated complex,[27] although no key intermediate species could be observed (Fig. 4).

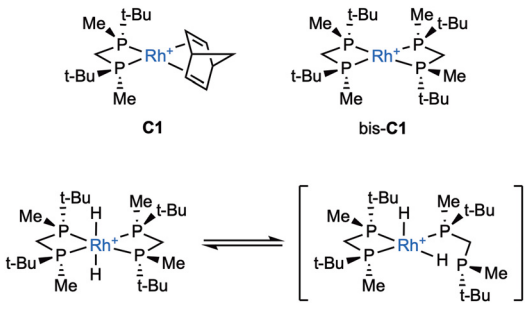


Fig. 4 Monochelated complex (**C1**) bischelated complex (bis-**C1**) (top). Equilibrium between the observed dihydrido species and the proposed hemilabile intermediate (bottom). Counter anions (PF_6^- or BF_4^-) have been omitted for clarity.

Shortly after the publication of the MiniPHOS ligands (**L1–L4**), a new *P*-stereogenic ligand was reported by Hoge and coworkers in 2004.[35] This diphosphane presented a C_1-symmetry, with only one *P*-stereogenic phosphorus, which bear a *t*-butyl and a methyl substituent—like MiniPHOS (**L1**)—, while the other phosphorus has two *t*-butyl substituents. Given that three out of the four substituents of the ligand were *t*-butyl, the ligand was named TriChickenFootPHOS (TCFP, **L8**). This design is of great interest because it follows a three-hindered quadrant strategy, where only one of the quadrants (the one with the non-bulky methyl substituent) of the catalyst is not sterically hindered. This fact allows for the preferential coordination of the catalytic substrates to form only one species, which could explain the great success of TCFP (**L8**) as a ligand for enantioselective hydrogenation (Fig. 5).[36,37] Interestingly, despite the resemblance with the MiniPHOS (**L1**) ligands, the synthesis of TCFP (**L8**) is completely different, since it was not prepared as an optically pure compound, but in racemic form and then the enantiomers of the diphosphane-borane were separated through preparative HPLC on a chiral stationary phase.

In terms of synthetic viability, the MiniPHOS (**L1–L7**) ligands have experienced an unforeseen problem that greatly affected their availability: the sudden and global shortage of sparteine as a cheap and easily available chiral auxiliary.[38,39] For this reason, Imamoto and coworkers developed in 2010 a new procedure that allowed for the gram-scale synthesis of optically pure *t*-butylmethylphosphane–borane using (−)-bornyl chloroformate as the chiral auxiliary, and allowing the obtention of both enantiomers through the inversion of the (*S*) enantiomer of the secondary phosphane-borane (Scheme 4).[27] Through this improved methodology, they were able to synthesize many ligands without relying on sparteine, like MiniPHOS (**L1–L7**), BisP*, or TCFP (**L8**), among many others.[27,31]

A few years after, Imamoto and coworkers reported a new methylene-bridged ligand, BulkyP* (**L9**, Scheme 4),[40] which resembled TCFP but exchanging the substituents of the non-*P*-stereogenic phosphorus from *t*-butyl to 1-adamantyl, furnishing a ligand with a much more pronounced steric effect, as its name implies. Thanks to this fact, the ligand turned out to be an air-stable, crystalline solid, making its handling more convenient. This ligand, like *t*-Bu-MiniPHOS (**L1**) and TCFP (**L8**), showed an excellent performance in the hydrogenation of functionalized alkenes (Fig. 5).

As it can be seen in Fig. 5, many short-bridged diphosphanes with a carbon backbone excel in the enantioselective hydrogenation reaction, proving their usefulness with a wide variety of conditions and substrates. The typical benchmark substrates (*Z*)-MAC, DMI and MAA have been hydrogenated with almost perfect enantioselectivity with many PCP ligands. The differences arise when more challenging substrates are explored, but *t*-Bu-MiniPhos (**L1**) and TCFP (**L8**) are especially outstanding among the broad range of ligands covered in this review. It seems clear that the rigidity of the four-membered chelate ring, and the electron-richness of the ligands are key

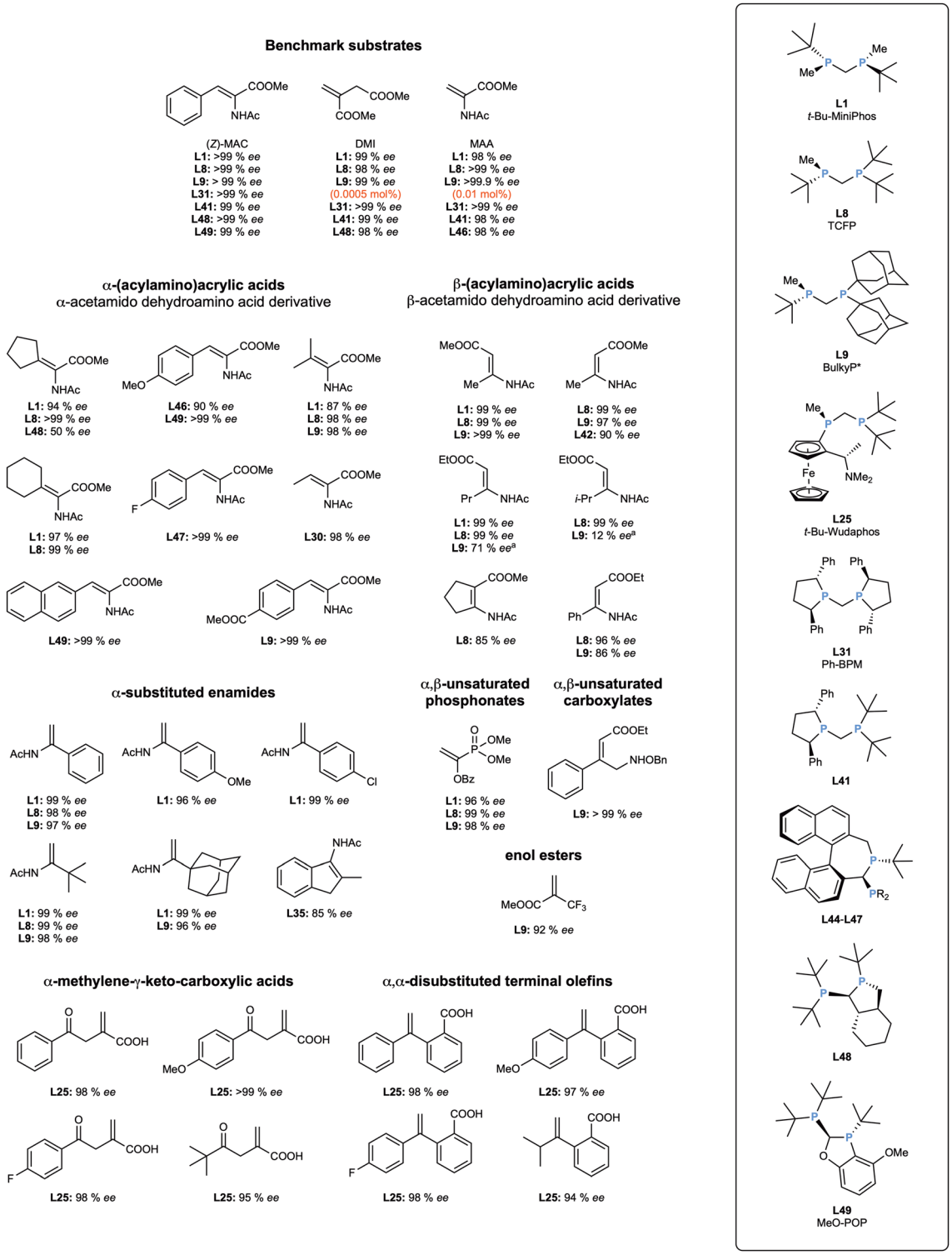
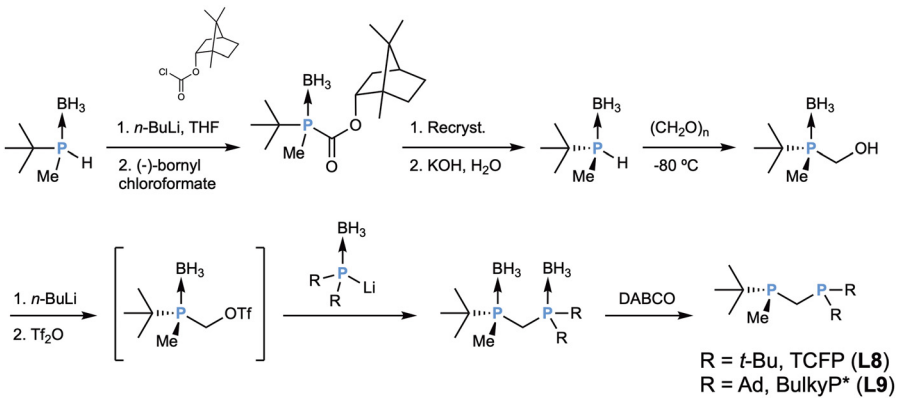


Fig. 5 Selected substrates used in Rh-catalysed enantioselective hydrogenation with PCP ligands and their corresponding enantioselectivities. [a] (*Z*)-isomer.

factors that produce very high enantioselectivities. It is notable that most of the best ligands contain the *t*-butyl substituent as a bulky, electron-releasing substituent for the phosphorus atom.

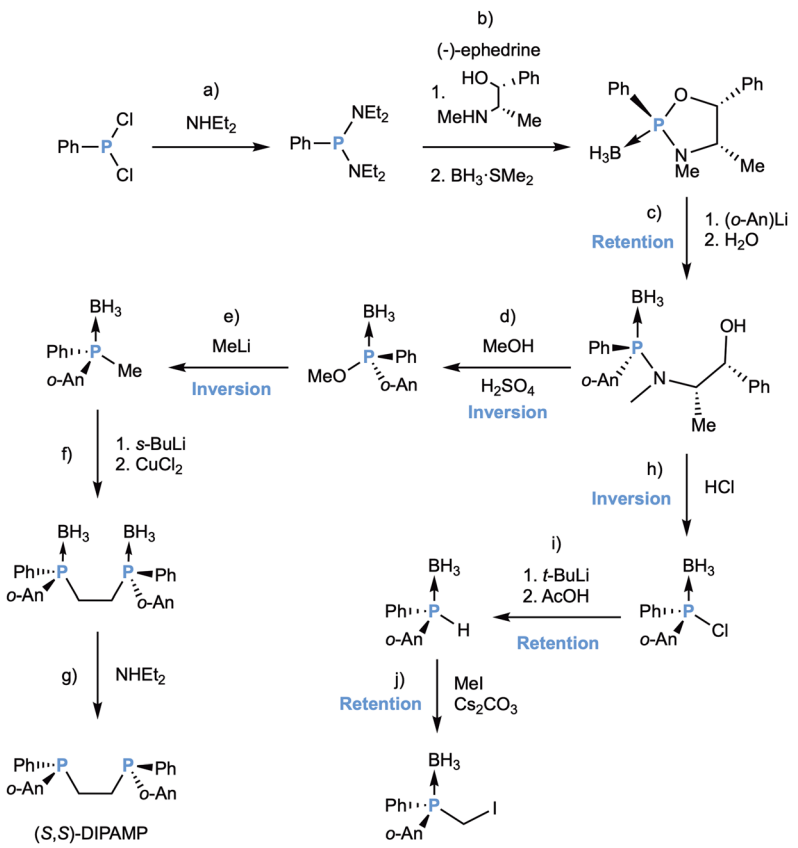
Aryl-substituted *P*-stereogenic diphosphanes. In 1990, Jugé and coworkers published a synthetic methodology to obtain *P*-stereogenic methylphenylarylphosphane–boranes with a very high optical purity.[41] This methodology, now known as the



Scheme 4 Synthesis of TCFP (**L8**) and BulkyP* (**L9**) ligands using (–)-bornyl chloroformate as a chiral auxiliary.

Jugé-Stephan method, has become one of the best ways to synthesize *P*-stereogenic compounds, providing an easy access to well-known ligands like DIPAMP (Scheme 5).[41]

The Jugé-Stephan method relies on the use of (1*R*,2*S*)-(–)-ephedrine or its enantiomer as the chiral auxiliary to confer the chirality on the phosphorus atom. Starting from $PhP(NEt_2)_2$, the addition of the ephedrine and borane generates a chiral intermediate oxazaphospholidine–borane (b), a heterocycle that is then selectively opened with an organolithium reagent (c), by P–O scission. After that, the P–N bond is cleaved through an acidic methanolysis (d), giving a *P*-stereogenic phosphinite-borane that can then be converted to a phosphane–borane with another organolithium reagent, in our case methyllithium (e). This product can be further reacted to synthesize a plethora of phosphorus compounds, or deprotected and coordinated as a monophosphane. In



Scheme 5 The original Jugé-Stephan methodology applied to the synthesis of (*S*,*S*)-DIPAMP (a–g). The opposite diastereomer could be obtained by switching the order of addition of the organolithium reagents (first MeLi and second (*o*-An)Li). Synthesis of *P*-stereogenic chlorophosphanes (h), secondary phosphanes (i), and iodomethylphosphanes (j).

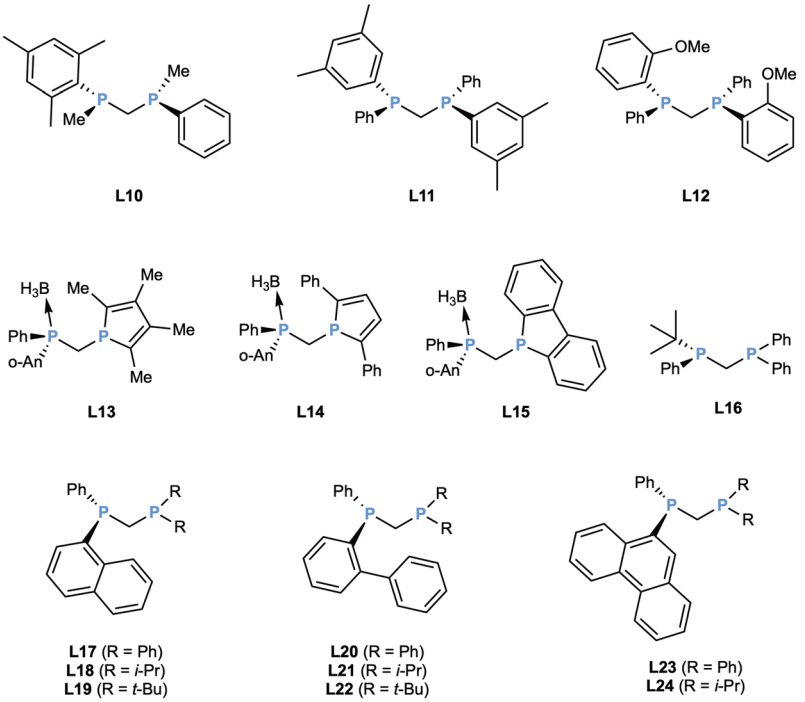


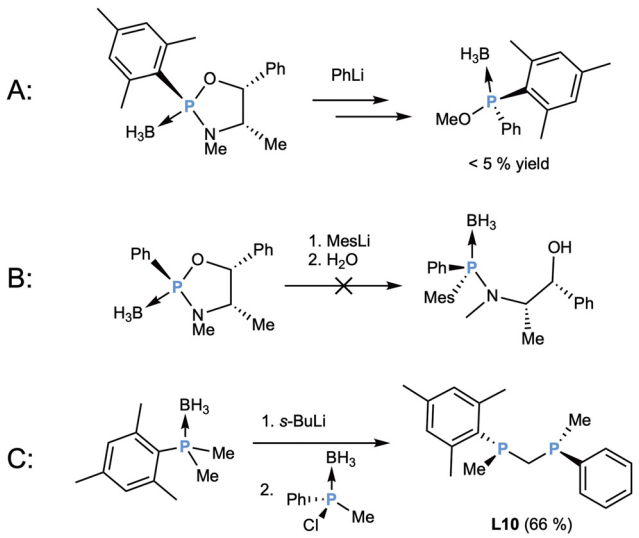
Fig. 6 Methylene-bridged PCP ligands prepared by the Jugé-Stephan method.

Scheme 5, the synthesis of DIPAMP[42]—an ethylene-bridged ligand—is depicted (f and g), which was the first diphosphane to be obtained through the Jugé-Stephan method.

This method can also be applied to the synthesis of methylene-bridged diphosphanes, since the methyl substituent of the starting phosphane–borane can be easily deprotonated and further reacted. In fact, 15 out of the 41 reported methylene-bridged chiral diphosphorus compounds have been synthesized following the Jugé-Stephan method (**L10–L24**, Fig. 6), showcasing the versatility of the procedure.

Out of the 15 described ligands obtained through the Jugé-Stephan method, the first one to be synthesized was **L10** by Mezzetti and coworkers in 2002.[43] In this contribution, the authors were exploring the synthesis of bulky *P*-stereogenic monophosphanes to obtain new highly symmetric, sterically hindered ligands. Initially, the synthesis of mesitylmethylphenylphosphane-borane was attempted, but it could only be obtained if the mesityl substituent was introduced first into the oxazaphospholidine–borane ring (Scheme 5b), and the phenyl substituent was introduced in the second place (c). Regardless of this, the yields were very low, making the procedure synthetically unsuitable (Scheme 6A). If the reaction was performed inverting the order of these reagents, no product was formed, probably due to the steric hindrance of the mesityllithium reagent (Scheme 6B).

For this reason, the focus was shifted towards the non-chiral mesityldimethylphosphane-borane, which was obtained in good yield, and it was deprotonated with *s*-BuLi and reacted with the chloromethylphenylphosphane-borane (Scheme 5h),[44] forming the new P–C bond. The optically active diastereomer



Scheme 6 (A and B) Attempted synthesis of mesitylmethylphenylphosphane-borane. (C) Synthesis of **L10**.

was formed with a good diastereomeric ratio in relation to the *meso* compound (83 : 17) and could be isolated in good yield and acceptable enantiopurity (86% ee) (Scheme 6C). Interestingly, when the ligand complexation with $[Rh(cod)_2]BF_4$ or $[Rh(nbd)_2]BF_4$ was attempted, no product was formed, but reacting the diphosphane with $[RhCl(cod)]_2$ in the presence of NH_4PF_6 afforded the expected $[Rh(cod)(\mathbf{L10})]PF_6$ (Fig. 7, Complex I). When testing the complex in the enantioselective hydrogenation reaction, the yields were low and the

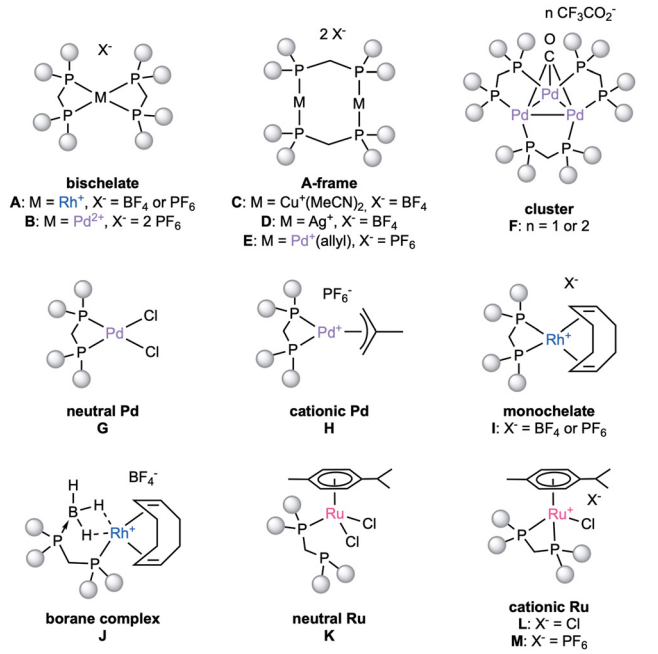


Fig. 7 General representation of the described complex types with methylene-bridged diphosphanes prepared by the Jugé-Stephan method.

obtained product was racemic, presumably due to the instability of the complex, which degraded giving metallic rhodium.

A few years later, Jugé and coworkers synthesized the dppm* ligands **L11** and **L12**, which were conceived as the *P*-stereogenic, optically pure variants of the classical ligand dppm.[45,46] Interestingly, these two are the only short-bridged ligands synthesized by the Jugé-Stephan methodology that are C_2-symmetric. This is because, as discussed in the synthesis of **L10**, the Jugé-Stephan methodology has limitations in terms of the substituents that can be introduced in the oxazaphospholidine–borane. On the other hand, the addition of another *P*-stereogenic moiety requires the use of a *P*-stereogenic chlorophosphane, which are synthetically challenging to obtain and handle in optically pure form due to configurational instability (Scheme 3h).[47,48]

Despite these limitations, Jugé and coworkers developed **L11**, where two of the phenyl groups of dppm are replaced by 3,5-dimethylphenyl (xylyl) groups, and **L12**, where *o*-anisyl groups were used instead. Besides, thanks to the versatility of the Jugé-Stephan methodology, both enantiomers of each ligand could be obtained since, in contrast to the Evans methodology, by altering the order of the substituents the opposite enantiomer could be obtained.

Interestingly, **L12** can be viewed as the methylene-bridged version of the well-known ligand DIPAMP, which is famous for its excellent catalytic results in the early days of enantioselective hydrogenation.[42] For this reason, it is surprising that the use of **L11** and **L12** as ligands for catalytic applications has not been reported. Instead, Jugé and coworkers studied their coordination properties to form C_3-symmetric trinuclear Pd clusters[45,46] (Fig. 7, Complex F) and 1D coordination polymers with Ag and Cu.[49] The monomers for these coordination polymers adopted what is known as an "A-frame" coordination (Fig. 7, Complexes C and D), which is not uncommon in coordination chemistry, and short-bridged ligands being no exception.[11]

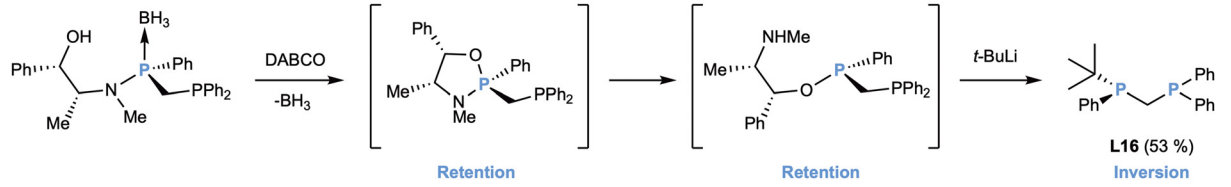
In 2021, Jugé and coworkers published a contribution where they combined a phospholyl moiety with a *P*-stereogenic fragment, connected through a methylene bridge (**L13–L15**).[50] These three compounds, which were later coordinated to rhodium(I), are not strictly diphosphanes, since the *P*-stereogenic atom remains boronated, and coordinates to the rhodium through the hydrogen atoms of the borane group, forming a 6-membered ring instead of the much more strained 4-membered ring from single-atom diphosphanes. Nonetheless, they have been included because they are relevant to the topic of chiral single-atom bridged diphosphorus ligands, both from their synthetic and coordination points of view.

The incorporation of the phospholyl moiety to the *P*-stereogenic fragment was performed starting either by reaction of deprotonated methylphosphane (Scheme 5e) with a cyanophosphole, furnishing ligands **L13–L15** or by the reaction of a iodomethylphosphane derived from the secondary phosphine-borane (Scheme 5i and j) with lithium phospholide, to give **L15**.

These ligands were coordinated to rhodium to yield complexes [Rh(L)(cod)]BF_4 (L = **L13–L15**), with the BH_3 coordinating to the Rh through two of its hydrogen atoms (η^2-BH_3) (Fig. 7, Complex J). When the complexes were tested in enantioselective hydrogenation with benchmark substrate methyl 2-acetamidoacrylate (MAA), their performance was not very good, with poor enantioselectivities (<20% ee) and low conversions in some cases. Although this represented the first case of a chiral κ^2-BH_3 coordinated complex used in enantioselective catalysis, the application of *P*-stereogenic phospholyl ligands in their more canonical, deboronated version has not been explored.

More recently, Jugé and coworkers have also developed a new methodology to obtain *P*-stereogenic phosphinites through an N → O phosphinyl migration.[51] This migration proceeded after the deboronation of the previously opened oxazaphospholidine–borane ring, *via* a phosphorane intermediate. Among the wide range of studied phosphanes, one example featuring the synthesis of a new methylene-bridged diphosphane **L16** was provided (Scheme 7), although its optical purity was not determined, and the ligand was not complexed or further studied.

Around the same time, our group also made a contribution to the field of *P*-stereogenic methylene-bridged diphosphanes.[52] In this initial article, we explored the synthesis of diphosphanes starting from optically pure *P*-stereogenic methylphosphane-boranes with 1-naphthyl, 2-biphenylyl, or 9-phenanthryl substituents, which were accessed through the Jugé-Stephan methodology (Scheme 5a–e) and had been used in hydrovinylation of olefins.[53] The boronated monopho-



Scheme 7 Synthesis of ligand **L16**. ee n.d.

sphanes could be easily deprotonated using an organolithium reagent and quenched with a chlorophosphane, in the same manner as with ligands **L10–L12**, but using achiral chlorophosphanes. This afforded a family of modular ligands comprised of aryl–aryl diphosphanes (**L17**, **L20**, and **L23**) and aryl–alkyl ones (**L18**, **L21**, and **L24**). This last group was later expanded with in a more recent contribution, where the *t*-butyl substituents were introduced (**L19** and **L22**).[29] In this case, it was observed that the bulkiness of the substituents allowed only for one of the phosphorus to be boronated after work-up. Interestingly, this phosphorus turned out to be that with the *t*-butyl substituents, after a spontaneous deboronation of the initially protected *P*-stereogenic phosphorus.

After deprotecting the ligands, their coordination with palladium(II) moieties was studied. Upon reacting them with [Pd(cod)Cl_2], the expected neutral complexes were obtained for diphosphanes **L17–L18**, **L20–L21**, and **L23–L24** (Fig. 7, Complex G).

After that, we wanted to explore their behaviour in cationic complexes, and the same ligands were thus coordinated to the metal precursor [Pd(μ-Cl)(η^3-allyl)]$_2$ in the presence of NH_4PF_6 acting as a halogen scavenger (Fig. 7, Complex H). The expected complexes could also be obtained, although it was observed that in the case of the aryl–aryl ligands, they were not the thermodynamically stable species. In solution, [Pd(η^3-allyl)(**L17**)]PF_6 quickly evolved into a dimeric, more complex A-frame species, where the diphosphane acted as a bridge between two different palladium atoms (Fig. 7, Complex E). This behaviour is probably favoured by the narrow bite angle and the four-membered chelate ring inherent to mononuclear complexes with short-bridged diphosphanes. In some cases, the geometry of the compound is so strained that the ligand adopts a hemilabile behaviour, decoordinating from the metal centre and favouring its coordination with a different palladium atom. Interestingly, aryl–alkyl diphosphanes did not form these A-frame complexes, suggesting that the coordination of the alkyl-substituted phosphorus with the palladium is stronger.

It was later observed that these A-frame complexes further decomposed into mononuclear bischelated and neutral [Pd(L)Cl_2] complexes. The bischelated complexes (Fig. 7, Complex B) are also common with short-bridged ligands. A crystal structure was obtained for the complex with **L19**, which was the first one obtained for a bischelated complex with a C_1-symmetric diphosphane, and it was interesting to see that the ligands presented a *cis* coordination, with the more sterically hindered substituents on the same side. This unexpected behaviour (from a steric point of view) could also be observed with the analogous rhodium(I) complex bearing ligand **L20**.[29]

After palladium, the coordination of these ligands to ruthenium and rhodium was also explored. **L20** and **L21** were reacted with [RuCl(μ-Cl)(η^6-*p*-cymene)]$_2$ in the presence of a halogen scavenger. Interestingly, the substituents on the non-*P*-stereogenic phosphorus greatly influenced the coordination behaviour of the ligands, as had been observed with palladium. In the case of ruthenium, **L21** showed a much more pronounced trend to form chelated complexes, forming the cationic complex even when no halogen scavenger was added, with one of the chlorines acting as the counteranion (Fig. 7, Complex L). When NH_4PF_6 was used, the expected complex was obtained (Fig. 7, Complex M). On the other hand, applying these same conditions to **L20** produced the neutral complex with the ligand acting in a hemilabile fashion, with only the non-*P*-stereogenic phosphorus coordinated to the ruthenium (Fig. 7, Complex K). Only when the stronger halogen scavenger $TlPF_6$ was used the chelated cationic complex was observed. However, it was also determined that the solvent plays a key role in the coordination of these ligands, since it was noticed that the hemilabile complex turned into the corresponding chelate when dissolved in methanol.[54]

In the case of rhodium, a more predictable behaviour can be observed for ligands **L17–L22**, since depending on the equivalents of ligands employed with respect to rhodium, both the bischelated (Fig. 7, Complex A) or monochelated complexes (Fig. 7, Complex I) could be obtained starting from metal precursor [Rh(cod)$_2$]BF_4. Contrasting with what had been reported by Imamoto and coworkers for **L1**,[31] the diene of the precursor did not influence the final coordination of the rhodium, and neither did the counteranion, as had been reported by Mezzetti and coworkers for ligand **L10**.[43] Instead, the monochelated/bischelated behaviour could be regulated by carefully controlling the stoichiometry, order and addition rate of the reagents. When a solution of the rhodium precursor was added dropwise on a solution of the diphosphane solution, the bischelate was preferentially formed. On the other hand, if the solution of the ligand was added dropwise to a solution of the rhodium complex, the pure monochelated complexes could be obtained.

The rhodium monochelated complexes of ligands **L17–L22**, as well as the bischelate of **L21**, were tested as catalysts in the enantioselective hydrogenation reaction. Almost all complexes showed quantitative conversions to the desired products, but enantioselectivities were moderate at best (<50% ee).

Around the same time, Dong, Zhang, and coworkers developed the new methylene bridged diphosphane **L25** with a *P*-stereogenic phosphorus substituted by a chiral ferrocenyl moiety.[55] The rationale behind this design was to follow the three-hindered quadrant strategy which had produced successful results with some ligands, like the aforementioned TCFP (**L8**).[35] Additionally, this new ligand **L25**, nicknamed *t*-Bu-Wudaphos, would have the advantage of being easier to synthesize and to handle, since it makes use of Ugi's amine as a more convenient way of introducing a chiral motif into the molecule.

The synthesis of the ligand proceeded by deprotonation of the *ortho* position of the substituted cyclopentadienyl of ferrocene, which was then reacted with PCl_3 to introduce the first phosphorus atom, which will become the *P*-stereogenic centre. After that, the boronated di-*t*-butylmethylphosphane was lithiated and added to the mixture, reacting with one of the two remaining chlorines of the initial PCl_3 and forming the methylene bridge through a phosphination reaction. Finally, the last chlorine was reacted with methylmagnesium chloride to give the partially boronated ligand as a single diastereomer, thanks to the use of the optically pure Ugi's amine as a chiral auxiliary. After deprotection, the final ligand **L25** is obtained as a convenient highly air-stable solid (Scheme 8).

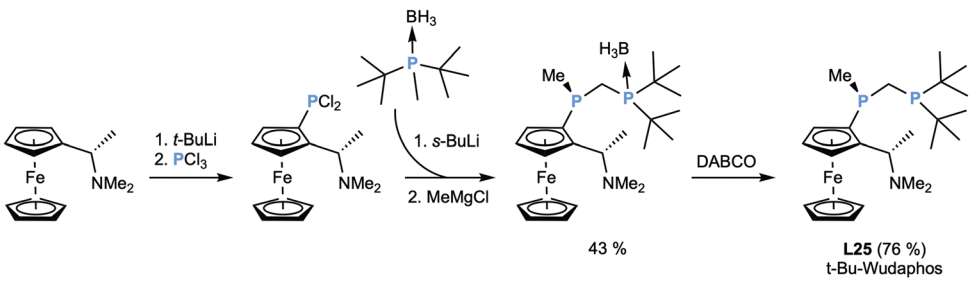
Unfortunately, no coordination studies for this interesting ligand have been described, but it was used *in situ* with $[Rh(nbd)_2]BF_4$ to assess its catalytic performance in enantioselective hydrogenation. The chosen substrates were α-methylene-γ-keto-carboxylic acids due to their acidic nature. It was postulated that the amine of the Ugi's base could interact with acidic substrates through ion pair noncovalent interactions, directing even more the selective coordination of the substrate to the rhodium complex, in addition to the previously mentioned three hindered quadrant strategy. When a varied scope of carboxylic acids was tested, it was observed that the hydrogenations proceeded with excellent enantioselectivities and conversions with a wide variety of substituents (Fig. 5). On the other hand, when the proposed ion pair interaction was disrupted by adding either an external base, or by removing the acidic group from the substrate, a substantial drop in either conversion or enantioselectivity was observed, highlighting the critical role that this interaction plays in the reaction.

Additionally, α,α-disubstituted terminal olefins were also tested as substrates, which resulted in a more challenging substrate due to the similarity of the olefin substituents.[56] However, thanks to the ion pair effect, the interaction between the carboxylic acid and the amine could be used to direct the coordination of the olefin, resulting in excellent yields and enantioselectivities (Fig. 5).

Methylene-bridged non-*P*-stereogenic diphosphanes

The same year that the MiniPHOS ligands (**L1–L4**) were disclosed by Imamoto,[25] Werner and coworkers also published a very interesting contribution which explored the synthesis of C_2- and C_1-symmetric methylene bridged diphosphanes.[57] Although the focus of their work was not set on obtaining chiral compounds, four out of the eleven ligands that they developed contained the chiral substituent (*R*)-menthyl, which conferred optical purity to the compounds (**L26–L29**). The synthesis of these diphosphanes proceeded using stannylated iodomethanes ICH_2SnR_3 (R = Ph, Me) as starting materials. By reacting these compounds with *n*-BuLi and dimenthylchlorophosphane, Men_2PCH_2SnR could be obtained (Men = menthyl). Then, addition of an organolithium reagent results in a transmetallation, producing SnR_4 and the lithiated phosphane, which was then reacted with the appropriate chlorophosphane R'_2PCl to produce ligands **L26** (R′ = Men), **L27** (R′ = i-Pr), **L28** (R′ = Cy), and **L29** (R′ = Ph). Out of the four synthesized ligands, only **L26** presents C_2 symmetry, with all the substituents on both phosphorus being menthyl groups. It is interesting to note that, in the same contribution, the synthesis arsinophosphanes was also explored, and the first crystal structure of a chiral compound of this kind was obtained for the ligand $Men_2PCH_2AsCy_2$.[57]

After that, the coordination to rhodium(I) of various diphosphanes and arsinophosphanes was explored, although unfortunately none of the chiral ligands **L26–L29** were studied. Nonetheless, the typical coordinative behaviour of achiral, methylene-bridged diphosphanes was observed, obtaining bischelated complexes, chloro-bridged dimers, and a η^6 coordination to benzene and toluene to Rh(I), similar to the catalytic systems that have been used by Willis, Weller, and coworkers for the hydroacylation reaction with short-bridged diphosphanes.[58,59] A few years later, in 2004, the Schrock-Osborn complexes [Rh(**L27**)(cod)]PF_6 and [Rh(**L29**)(cod)]PF_6



Scheme 8 Synthesis of **L25**, *t*-Bu-Wudaphos.

were synthesized by the same group and used as precatalysts in the enantioselective hydrogenation of α-acetamidocinnamic acid methylester, a functionalized trisubstituted olefin.[60] Although the reaction yielded the hydrogenated product quantitively, the enantioselectivities were moderate (29–69%) in all cases, regardless of the ligand and the reaction conditions.

Around the same time, Faraone and coworkers carried out a study on the effects of the bridging atom on short-bridged chiral diphosphanes, where they explored methylene, nitrogen and oxygen bridges.[61] To accomplish it, they synthesized C_2-symmetrical ligands with the phosphorus containing a binaphthyl moiety, which conferred the chirality to the system. In the case of the methylene-bridged ligand **L30**, the diphosphane was obtained by reacting bis(dichlorophosphino) methane with (*R*)-binaphthol (Fig. 8A). When coordinated to the Pd(η^3-1,3-diphenyallyl) precursor, it was observed that both monomeric and dimeric complexes were formed in solution (Fig. 8B). When the ligand was tested in the enantioselective allylic alkylation reaction, the resulting enantioselectivity was very low (<10% ee), probably due to the mixture of species formed in solution. It is interesting to note that, when these results are compared with the similar, ethylene-bridged counterpart of **L30** for the same reaction the performance was much better, achieving 90% conversion and 73% ee.[62] This poses the question of whether the more rigid 4-member chelate hindered the performance of **L30** in comparison with its more flexible, 5-member chelate analogue.

A few years later, Jackson and a coworker presented the ligand Ph-BPM **L31**,[63] which was conceived as a short-bridged version of the well-performant diphosphane Ph-BPE, with an ethylene bridge.[64] The diphospholane ligand was synthesized starting from the secondary phospholane–borane adduct, which was reacted with its mesylate-substituted derivative in the presence of *n*-BuLi to form the diboronated ligand, which could then be deprotected with DABCO yielding the final **L31** (Scheme 9A).

The [Rh(cod)(**L31**)]BF_4 was then obtained and used as a precatalyst in the enantioselective hydrogenation reaction, providing excellent conversions and enantioselectivities of benchmark substrates with catalysts loadings of as low as 0.01 mol% (Fig. 5). With these positive results, the ligand was also tested in ruthenium catalyzed imine hydrogenation, with overall good yields and selectivities, although not as good as in the previous reaction.

More recently, Pringle and coworkers developed a set of highly modular methylene-bridged diphosphanes with a chiral motif, that could be either a BINAP (**L32–L35**), a substituted BINAP (**L36–L37**), or an *ortho* substituted phospholane (**L38–L41**).[65] To synthesize them, the chiral chlorophosphane was reacted with $TMS(CH_2)PR_2$,[66] where R could be a phenyl, i-propyl, cyclohexyl, or a *t*-butyl substituent. With this flexible methodology, they were able to synthesize 10 new ligands using only a few different building blocks (Scheme 9B).

Interestingly, when coordination of these ligands to Rh was attempted with [Rh(nbd)$_2$]BF_4 or [Rh(cod)$_2$]BF_4 as metal precursors, only ligands **L38–L41**, which bore a phospholane moiety, were able to yield crystals suitable for X-ray diffraction. Ligands **L32–L37**, with a BINAP or BINAP-derived moiety, could only produce a crystal for when coordinated to Pt, obtaining the neutral complex [Pt(**L35**)Cl_2]. In both cases, the obtained structure corresponded to the ligand with *t*-butyl substituents, which seems to be a good substituent for crystallisation purposes.[29] Pringle and coworkers demonstrated the facile obtention of Rh complexes by performing, in a one-pot procedure, the synthesis of ligand **L41** and its complexation (Scheme 9B).

When the ligands were tested in the enantioselective hydrogenation of the three benchmark substrates MAC, MAA, and DMI, it was observed that the diphosphanes that gave the best enantioselectivities also had *t*-butyl substituents. Out of the 10 ligands used, **L41** turned out to be the best performing one with the studied conditions (Fig. 5).

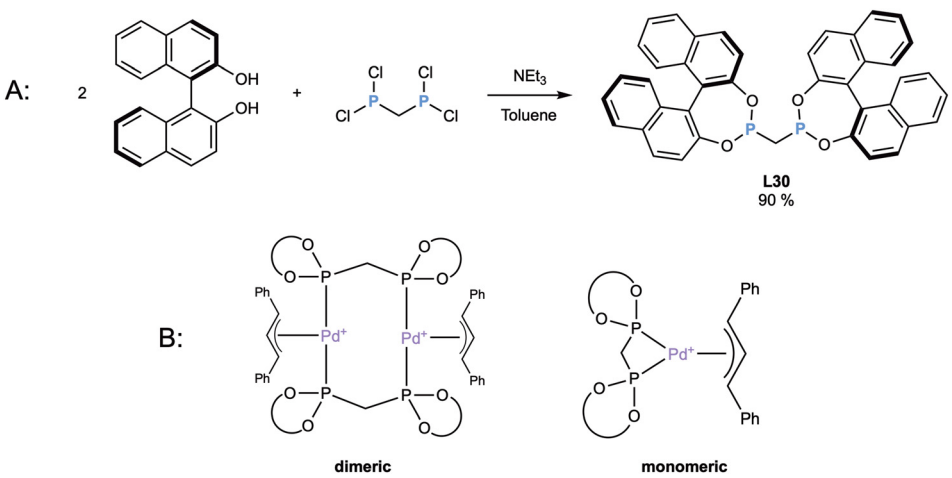
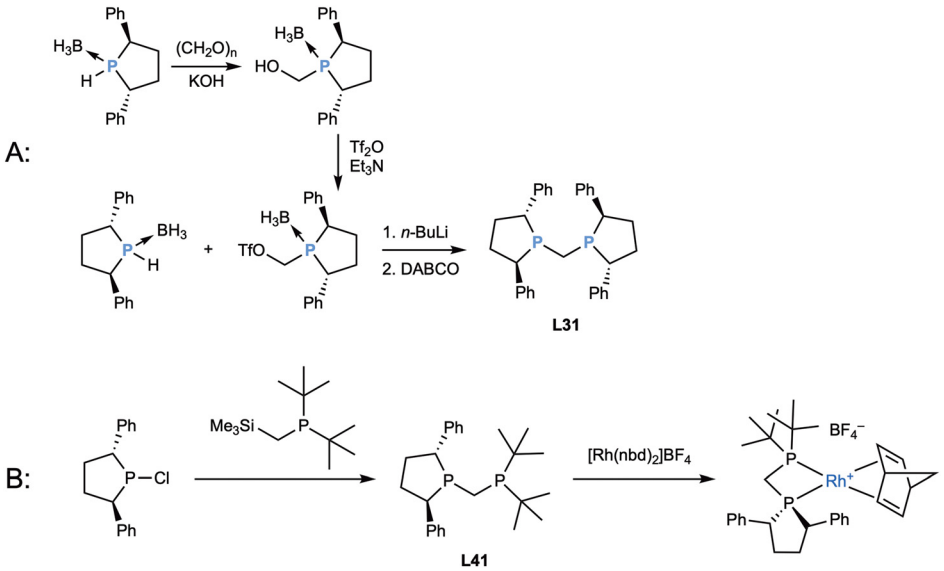


Fig. 8 (A) Synthesis of ligand **L30**. (B) Pd species observed in solution. PF_6^- counteranions have been omitted for clarity.



Scheme 9 (A) Synthesis of ligand **L31**. (B) One-pot synthesis and complexation of ligand **L41**. The same procedure is applied for the synthesis of ligands **L32–L41**.

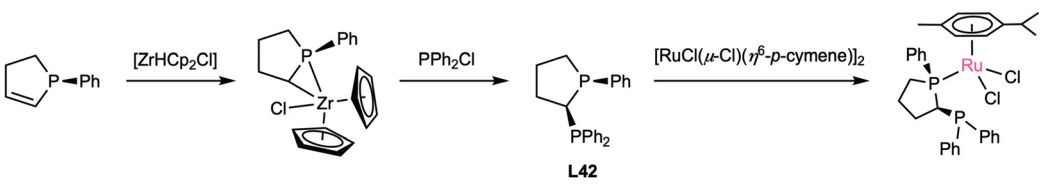
Diphosphanes with a substituted methylene bridge

In 1995, Pietrusiewicz, Majoral, and coworkers developed the first chiral short-bridged diphosphane with a substituted carbon bridge.[67] This ligand **L42** was achieved through a very unconventional reaction involving a P–Zr adduct. Starting from the optically pure (*R*)-1-phenyl-2,5-dihydrophosphole, the addition of [Cp_2ZrHCl] resulted in the formation of a chiral α-zirconated phospholane complex. After that, addition of PPh_2Cl cleaved the Zr–C bond, resulting in the final diphosphane through an inversion of configuration at the carbon centre.[67,68] This ligand was later coordinated with the typical Ru precursor [$RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ to form a hemilabile complex (Scheme 10). The complexed ligand was then further derivatized either by oxidising the uncoordinated phosphorus or by imination through a Staudinger reaction, obtaining a P(III)–P(V) ligand. This derivatized complexes were tested as catalysts in the Diels–Alder reaction, providing good activity but low to moderate diastereo- and enantioselectivity.[69] However, the basic **L42** ligand has never been studied in catalysis.

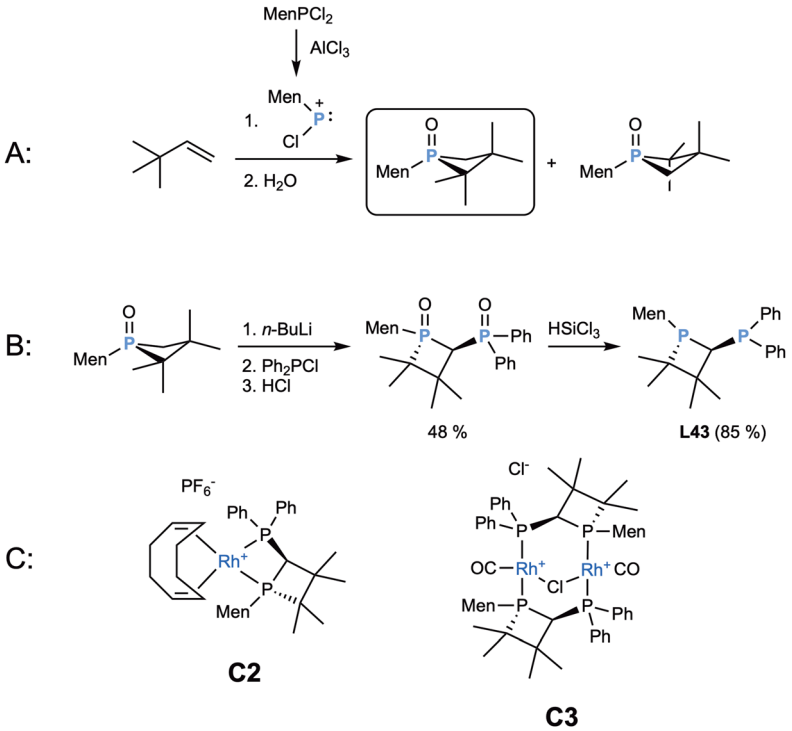
That same year, the alkyl-substituted, short-bridged ligand **L43** was developed by Marinetti and coworkers.[70] This ligand is very interesting because it makes use of a four-membered phosphorus heterocycle (phosphetane)[71] to provide the carbon atom for the ligand bridge. This uncommon structure was obtained by deprotonating the phosphetane oxide with *n*-butyllithium and reacting the carbanion with diphenylchlorophosphane oxide, to give the oxidized diphosphane, which was then reduced with trichlorosilane maintaining the optical purity (Scheme 11B). The initial phosphetane oxide was obtained through the classical McBride method, where a phosphenium cation is formed by the reaction of a dichlorophosphane with $AlCl_3$, which is then reacted with *t*-butyl ethylene to give the final phosphetane through a rearrangement. In the work of Marinetti and coworkers,[70] the initial dichlorophosphane used was the optically pure dichloromenthylphosphane, which produced two different diastereomers that could be separated by fractional recrystallization,[72] providing the source of chirality for the final diphosphane (Scheme 11A).

This ligand **L43** was then coordinated to rhodium, obtaining the classical [Rh(cod)(**L10**)]PF_6 (**C2**) and a less common A-frame dinuclear structure with a bridging chlorine between the two Rh atoms **C3** (Scheme 11).

Shortly after, Zhang and coworkers developed a new family of ligands based on the binaphthyl motif.[20] It is interesting to note that, for these ligands, **L44–L47**, the initial alcohol groups of the BINOL were replaced by methyl groups, removing any heteroatoms (apart from phosphorus) from the mole-



Scheme 10 Synthesis and complexation of **L42**.



Scheme 11 (A) Synthesis of chiral phosphetane oxide. (B) Synthesis of ligand **L43**. (C) Rhodium complexes with ligand **L43**.

cule, which is quite an unusual feature for ligands featuring a BINAP moiety. In fact, Zhang and coworkers had previously developed the first account of a ligand with this fragment, the C_2-symmetric binapine, with a two-carbon bridge.[73] In the case of **L44–L47**, the unusual BINAP structure without oxygens allowed for the deprotonation of one of the carbon atoms adjacent to the phosphorus, to which a chlorophosphane could be linked to form the new P–C bond (Fig. 9, top).

After obtaining the ligands, the typical precatalysts of the type [Rh(cod)(L)]BF_4 could be obtained the four ligands **L44–L47**. When the complexes were tested in the enantioselective hydrogenation reaction, they generally provided good to excellent conversions and enantioselectivities when tested with α- and β-dehydroamino acid derivatives, and with α-arylenamides (Fig. 5). Interestingly, the catalytic reactions showed a strong dependence on the non-*P*-stereogenic phosphorus substituents, with the phenyl- and cyclohexyl-substituted diphosphanes (**L44** and **L46**, respectively) providing the best results. Unfortunately, no explanation for this behaviour could be provided, and no further studies have been carried out with these diphosphanes to try to elucidate this observation.

Around the same time, Zhang and coworkers also developed another chiral diphosphane with a substituted carbon bridge.[22] This new ligand **L48** was designed as a TCFP (**L8**) analogue, in a similar way to the previously mentioned *t*-Bu-Wudaphos **L25** (Scheme 8), which was also reported by Zhang and coworkers a few years later.[55] In the case of **L48**, however, the idea was to replace the *P*-stereogenic phosphorus with a *t*-butylphospholane fragment, expanding on the idea of the three hindered quadrant strategy. Similarly to what had been done with ligands **L44–L47**,[20] which were based on their predecessor binapine,[73] **L48** was based on the previous experience of the group with the diphospholane ZhangPhos.[74] By changing only the last synthetic step, the chiral monophospholane synthon could be reacted with *t*-butylchlorophosphane to obtain **L48** (Fig. 9, middle).

After that, the ligand was tested in enantioselective hydrogenation of the typical benchmark substrates and a wide scope of derivatives, giving full conversions and >94% ee in the 25 substrates tested, with 15 of them presenting 99% ee or more (Fig. 5).

The same year, Tang and coworkers published a contribution where they presented a new family of ligands, with a structural similarity to the previously discussed **L48**, but with very different electronic properties, since the phospholane was changed by an oxaphospholane, and the attached cyclohexyl was instead a phenyl.[21] On top of that, they studied how different substituents on the non-*P*-stereogenic phosphorus and on the *ortho* position of the phenyl ring could affect the catalytic performance of the ligands, developing four variants **L49–L52**. The strategy followed was similar to the one that Zhang and coworkers also used for **L44–L48**, where one cyclic monophosphane could be used to obtain the C_2-symmetric ligand (in the case of Tang and coworkers, the well-performing BIBOP),[75] or the C_1-symmetric short-bridged one (Fig. 9, bottom). In this case, the synthesis proceeded in a similar way as with **L44–L49**, where the P-adjacent carbon was deprotonated with an organolithium and reacted with a chloropho-

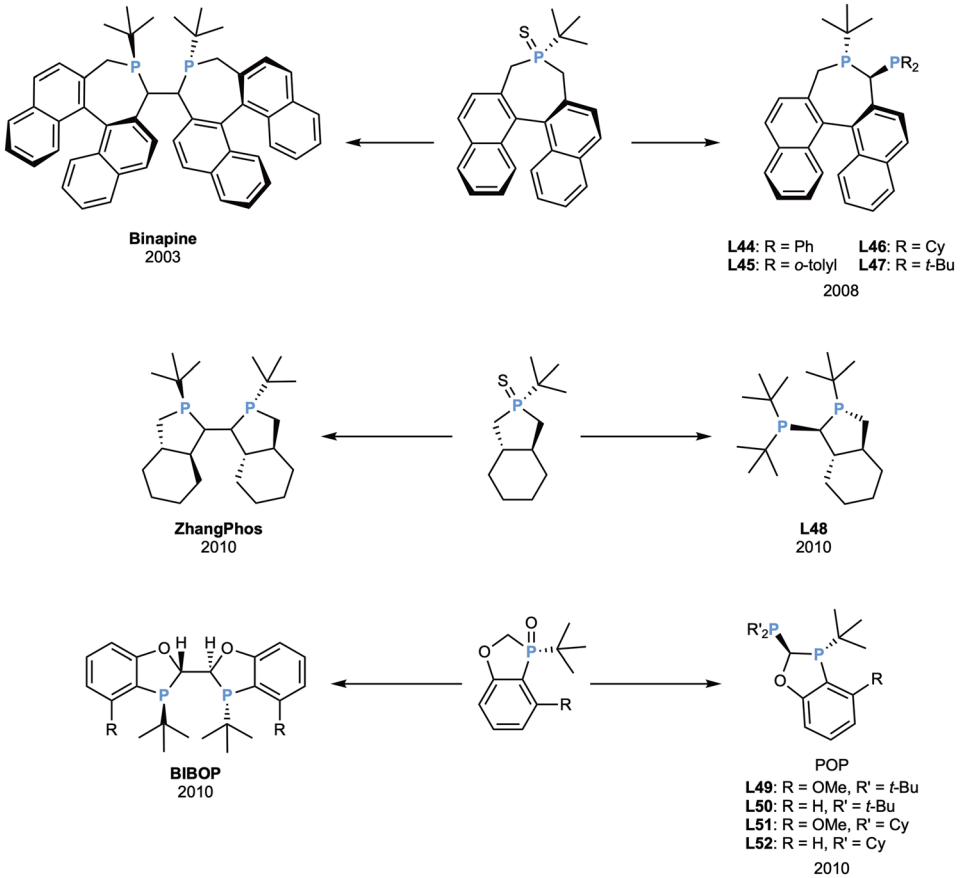


Fig. 9 Cyclic monophosphanes (middle), C_2-symmetric, ethylene-bridged diphosphanes (left) and C_1-symmetric, methylene-bridged diphosphanes (right).

sphane. The ligands were named POPs, with **L49** specifically known as MeO-POP, since it was the one that performed best.

Initially, the ligands were coordinated to $[Rh(nbd)_2]BF_4$ to obtain the classical precursors $[Rh(L)(nbd)]BF_4$ without issues. Interestingly, an X-ray crystal structure of the complex with MeO-POP (**L49**) could be obtained, where a bite angle of 73.7° could be observed. This value is bigger than the typical ~72° bite angle observed for short-bridged ligands with a carbon bridge, a fact that is probably explained by rigidity and steric hindrance imposed by the bicyclic bridge, on top of the already bulky *t*-butyl substituents of the phosphorus. When the complexes were tested in the enantioselective hydrogenation of 2-acetamido-3-phenylacrylic acid, it was observed that MeO-POP was clearly the ligand providing the highest enantioselectivity (99% ee), while its counterpart with cyclohexyl substituents, **L51**, was by far the worst performing one (54% ee). On the other hand, **L50** and **L52** showed very similar selectivities (87% and 92% ee, respectively), indicating that the methoxy substituent of the phenyl ring attached to the oxaphospholane played a pivotal role in the catalysis. Unfortunately, the mechanistic underpinnings behind this observation have not been explored. Instead, efforts were focused on expanding the substrate scope of the catalysis, showing that the ligands were especially well-suited for hydrogenating β-(acylamino) acrylates, both as (*E*)- and (*Z*)-isomers (Fig. 5).

N-bridged diphosphorus ligands (PNP)

Several outstanding ligands with a carbon bridge have been described in the previous section. Most of them contain an unsubstituted methylene bridge (Scheme 1, groups and 2) because the preparation of chiral diphosphanes with a substituted methylene bridge, although leading to interesting diphosphanes (Scheme 1, group 3), is by no means straightforward.

Changing the bridging atom from carbon to nitrogen opens a completely different scenario,[76] giving PNP ligands that are often called diphosphazanes.[77–80] The "*parent*" compound would be bis(diphenylphosphino)amine (dppa),[81] which is analogous to dppm but with a NH bridge and was described for the first time almost 60 years ago.[82,83]

The NH bridge can be deprotonated to create anionic ligands or, more importantly for the purpose of the present perspective, alkylated with a group, which can be chiral, providing an easy entry to chiral PNP ligands. This has given many ligands (32 in total, **L53**, **L56–L86**, Fig. 3), described in

the following sections. Interestingly, unsubstituted, chiral NH-bridged ligands were unknown in the literature, until the relatively recent discovery of the important *P*-stereogenic ligand MaxPHOS in 2010,[84] described in the next section.

Unsubstituted nitrogen bridge

The large steric bias between the *t*-butyl and methyl groups, along with the rigid backbone of a methylene bridge has given PCP ligands producing exceptionally high enantioselectivities in enantioselective catalysis,[85] as seen in the previous sections. These ligands are prepared by several methods, but important synthons are *t*-butylmethylphosphane-borane and *t*-butyldimethylphosphane-borane, both of nucleophilic character after deprotonation.

Inspired by this chemistry, the group of Riera and Verdaguer[86] envisaged that the aminophosphino-borane **P1** and the phosphinous acid-borane **P2** could be convenient electrophilic synthons for the preparation of new ligands (Fig. 10) with the *t*-butyl/methyl substituents. It should be recalled that their most logical precursors, chlorophosphanes, are difficult to obtain in optically pure form, due to lack of configurational stability.[47]

Inspired by early work of Kolodiazhnyi[87] racemic *t*-butylchlorophosphanes were reacted with several enantiopure amines, followed by boronation, producing the corresponding aminophosphane-boranes in low diastereomeric ratios, by a partial DKR process (Scheme 12).[84]

Fortunately, in the case of phenylglycinamide, the two diastereomers of the *t*-butylmethylaminophosphane-borane could be separated by column chromatography and recrystallization. A reductive cleavage with lithium in liquid ammonia furnished the aminophosphane-borane **P1** as stable and crystalline solid.

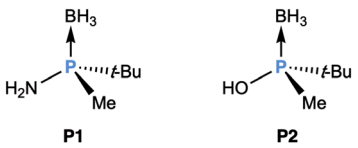
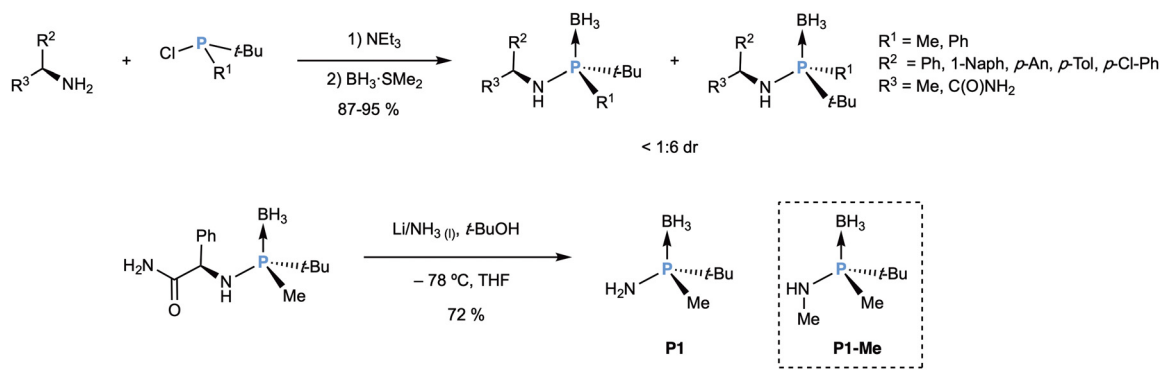


Fig. 10 Structures of amino *t*-butylmethylphosphane-borane (**P1**) and *t*-butylmethylphosphinous acid-borane (**P2**).

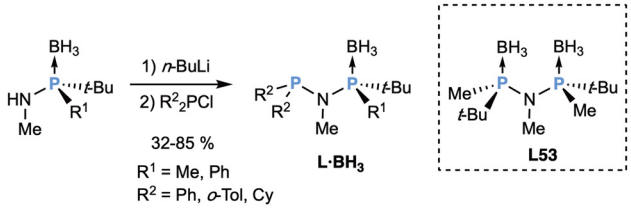
The *N*-methylated compound (**P1-Me**) could be also prepared by methylation of **P1**. The compounds **P1** and **P1-Me** are ideal building blocks for enantiopure P*NP and P*NP* ligands (P* denotes a *P*-stereogenic moiety) and this was exploited with the preparation of several *N*-methyl substituted diphosphazane-boranes (**L·BH$_3$**) by deprotonation and reaction with a chlorophosphane (Scheme 13).

Interestingly, the reaction with racemic *t*-BuMePCl furnished a mixture of *meso*- and C_2-symmetric **L53**, which can be considered a nitrogen (*methylated* nitrogen) analogue of the ligand *t*-Bu-MiniPHOS (**L1**),[25,32] discussed earlier in this review (Scheme 3). The reaction with the bulkier *t*-Bu$_2$PCl only took place with the primary amine of **P1** and furnished the so-called ligand MaxPHOS (**L54**), named after their discoverers, as shown in Scheme 14.[88]

The reaction of deprotonated **P1** with *t*-Bu$_2$PCl produced **L54·BH$_3$**, a phosphamide that was exclusively present as the P–H tautomer (formally, a P(v)–P(iii) species) as shown in scheme, which prevented the oxidation of the phosphorus atom. The deboronation with tetrafluoroboric acid was possible only under rather harsh conditions, which did not hydrolyse the P–N bonds and rendered the phosphonium salt (**L54·HBF$_4$**) as a very crystalline, air-stable solid, soluble in medium and high-polarity solvents. The description of the electronic structure of this compound corresponds to a hybrid form between the tautomeric forms of the scheme, since the two P–N distances were found to be almost identical by X-ray crystallography.[88] The free MaxPHOS (**L54**) ligand could be obtained in a later publication[88] by deprotonation of MaxPHOS·BH$_3$ (**L54·HBF$_4$**) at low temperature with *n*-BuLi, as a very air-sensitive oil. For this reason, in the complexation reactions the salt is usually used, as discussed later. Notably, the free ligand behaves as the NH tautomer, in contrast to the related ligand (*t*-Bu)$_2$PNHP(*t*-Bu)$_2$, which is present in a 70 : 30 mixture of the NH and PH tautomers, respectively, in toluene solution.[89] In this regard, switching a single *t*-butyl group to a methyl is enough to displace completely the tautomeric equilibrium towards the NH form. Interestingly, MaxPHOS (**L54**) ligand can be considered the analogous of Hoge's TCFP (**L8**) ligand (Scheme 4),[35] replacing the methylene bridge with a NH bridge.



Scheme 12 Preparation of diastereomeric mixtures of aminophosphane-boranes and first reported preparation of **P1** and **P1-Me**.



Scheme 13 Preparation of *N*-methyl substituted diphosphazane-boranes (**L·BH$_3$**).

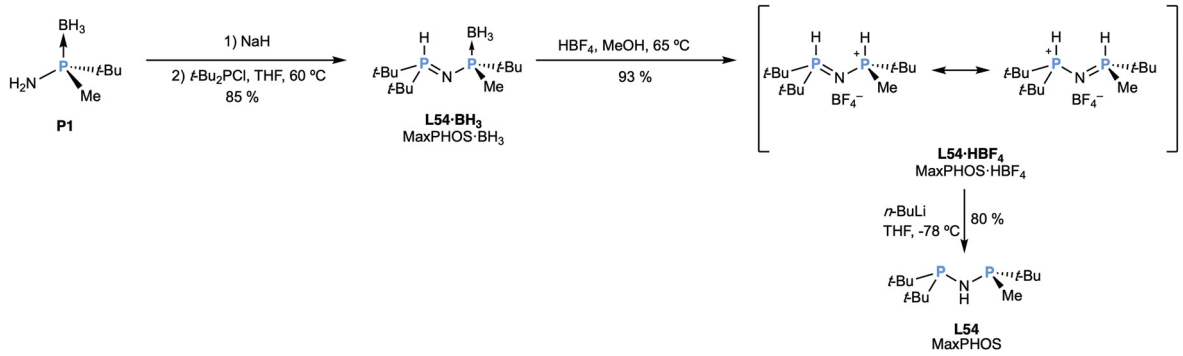
Very recently,[90] the same group has used the same synthetic methodology to prepare the so-called MAdPHOS ligand (**L55**), bearing two 1-adamantyl groups in the non-stereogenic phosphorus atom (Scheme 15).

This ligand was prepared because of the beneficial effects of 1-adamantyl groups as phosphorus substituent,[91] demonstrated by Imamoto with his BulkyP*(**L9**) ligand (Scheme 4),[40] which resulted to be solid and air-stable, compared to the very air-sensitive TCFP (**L8**, Scheme 4), bearing *t*-butyl groups.

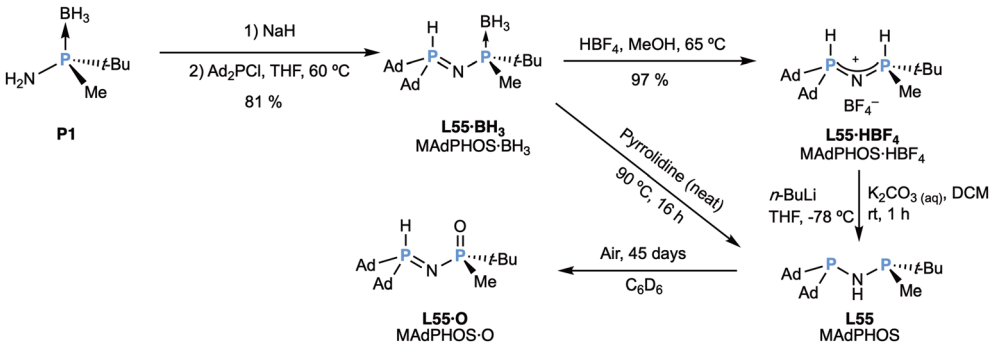
The precursors MAdPHOS·BH$_3$ (**L55·BH$_3$**) and MAdPHOS·HBF$_4$ (**L55·HBF$_4$**) were prepared (Scheme 15) in an analogous way to the MaxPHOS (**L54**) precursors (Scheme 14). The same bonding situation was encountered according to NMR spectroscopy. Free MAdPHOS (**L55**) could be obtained by deprotonation of MAdPHOS·HBF$_4$ (**L55·HBF$_4$**) with *n*-BuLi, as MaxPHOS (**L54**, Scheme 14), but also with the much milder base potassium carbonate. Interestingly, the ligand could also be obtained by deboronation of MAdPHOS·BH$_3$ (**L55·BH$_3$**) with pyrrolidine, but in this case the pyrrolidine-borane adduct could not be separated from the ligand. Importantly, free MAdPHOS (**L55**) is much more stable than MaxPHOS (**L54**), because it could be stored in the fridge (under nitrogen atmosphere) for 2 months. A sample in an NMR tube in benzene slowly oxidized (45 days) to give exclusively MAdPHOS·O (**L55·O**), the imino-tautomer with the non-stereogenic phosphorus as a P–H species and the stereogenic phosphorus oxidized.

Both MaxPHOS (**L54**) and MAdPHOS (**L55**) were initially developed as chiral ligands for rhodium-catalyzed hydrogenation, inspired by the TCFP (**L8**) and BulkyP* (**L9**) ligands, respectively. For this reason, the coordination of the ligands to rhodium(I) moieties has been well studied (Scheme 16).

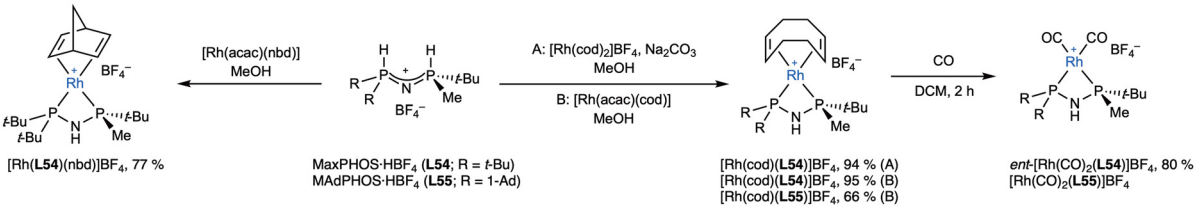
Initially, the very stable Schrock-Osborn complex [Rh(cod)(**L54**)]BF$_4$ was prepared by reaction of the MaxPHOS (**L54·HBF$_4$**) salt with [Rh(cod)$_2$]BF$_4$ precursor with sodium carbonate to neutralize the equivalent of acid formed (procedure A).[84] This method worked well, but a simplified method (procedure B) was developed, which took advantage of the basicity of the departing acetylacetonate ligand[92] present in the precur-



Scheme 14 Synthesis of the MaxPHOS ligand (**L54**).



Scheme 15 Preparation of the MAdPHOS (**L55**) ligand.



Scheme 16 Rhodium(I) complexes of MaxPHOS (**L54**) and MAdPHOS (**L55**).

sor [Rh(acac)(cod)] to avoid the formation of any salt.[88] The same method was employed very recently with the MAdPHOS (**L55**) ligand with good results.[90] An analogous method was used to prepare [Rh(**L54**)(nbd)]BF_4, although this complex was found to be unstable.[88] In order to evaluate the electronic features of MaxPHOS (**L54**) and MAdPHOS (**L55**), the dicarbonyl complexes were easily obtained as yellow solids by displacement of cod under CO atmosphere (Scheme 16). In addition, the selenides of the two ligands were also prepared by treatment of the free ligands with selenium, to measure the $^1J(^{31}P,^{77}Se)$, which is a measure of the σ-donation of phosphorus ligands.[93–95]

Some important parameters of MaxPHOS (**L54**) and MAdPHOS (**L55**), their related methylene-bridged diphosphanes (TCFP (**L8**) and BulkyP* (**L9**), respectively; Scheme 4) and the rhodium(I) complexes are given in Table 1.

The ^{31}P–^{77}Se coupling constant, although it is not free from steric interreference,[88] is indicative of the σ-donation of phosphanes, with electron-richer ligands giving smaller coupling constants.[95] From the table it can be concluded that the σ-donor capacity follows the order TCFP (**L8**) > BulkyP* (**L9**) > MAdPHOS (**L55**) > MaxPHOS (**L54**).

From the frequency of the CO stretching vibration (the smaller the value, the higher the σ-donation),[97] the order would be TCFP (**L8**) ≈ MAdPHOS (**L55**) > MaxPHOS (**L54**). It seems clear, therefore, that electron withdrawing inductive effect of the NH bridge makes the MaxPHOS (**L54**) and MAdPHOS (**L55**) less σ-donating than TCFP (**L8**) and BulkyP* (**L9**).

Table 1 Important parameters of TCFP(**L8**), BulkyP* (**L9**), MaxPHOS (**L54**) and MadPhos (**L55**)

Ligand or complex	Bite angle (°)	ν_{Cos} (cm^{-1})	$^1J_{P-Se}$ (Hz)	Ref.
TCPF (**L8**)	—	—	723, 713	88
MaxPHOS (**L54**)	—	—	776, 740	88
BulkyP* (**L9**)	—	—	723, 723	96
MAdPHOS (**L55**)	—	—	766, 736	90
[Rh(**L8**)(cod)]BF_4	72.6	—	—	35
[Rh(**L9**)(cod)]SbF_6	72.5	—	—	40
[Rh(**L54**)(cod)]]BF_4	70.0	—	—	84
[Rh(**L54**)(nbd)]BF_4	70.1	—	—	88
[Rh(**L55**)(cod)]BF_4	70.5	—	—	90
[Rh(**L8**)$(CO)_2$]BF_4	—	2079	—	88
[Rh(**L54**)$(CO)_2$]BF_4	69.7	2088	—	88 and 90
[Rh(**L55**)$(CO)_2$]BF_4	—	2079	—	90

Both MaxPHOS (**L54**) and MAdPHOS (**L55**) performed very well in enantioselective hydrogenation of wide range of functionalised olefins under mild conditions (Fig. 11).[10,86,88,90]

The substrates included the benchmark dehydroaminoacids, alkenes containing heteroaryl substituents and many different *N*-protecting groups and enamides. In some cases, the performance of the two ligands was similar, but in others the bulkier ligand MAdPHOS (**L55**) outperformed MaxPHOS (**L54**).[10,90]

A rhodium complex of MaxPHOS (**L54**) was also studied by the same group[98] as catalytic precursors for the intramolecular Pauson-Khand reaction of 1,6-enynes (Scheme 17).

The reaction provided moderate yields of the desired Pauson-Khand (PK) adduct achieving good enantioselectivities, under low CO pressure. A competitive reaction was the [2 + 2 + 2] cycloaddition between the enyne and the triple bond of another enyne. The dicarbonyl complex (Scheme 16) was shown to be catalytically active and was used to demonstrate that the presence of cod was important to attain high selectivity.

The complexation of MaxPHOS (**L54**) to nickel(II) and palladium(II) moieties has also been explored by Grabulosa, Verdaguer and coworkers.[99] The coordination chemistry was explored with simple nickel(II) and palladium(II) precursors (Scheme 18).

The reaction of the MaxPHOS salt (**L54·HBF$_4$**) with [M$(acac)_2$] (M = Ni, Pd), following the "acac method"[92] cleanly yielded the pure complexes as air-stable solids, whose X-ray structures were very similar except for the coordination distances. In the same report, the preparation of the neutral dihalido complexes of palladium(II) were reported. While the dibromido complex could be obtained from palladium acetate in the presence of sodium bromide, the method did not work for the preparation of the diclorido complex, which had to be prepared from the free ligand and [$PdCl_2$(cod)].

The reaction of three different η^3-allylic palladium(II) dimers with MaxPHOS·HBF_4 (**L54·HBF$_4$**) in the presence of sodium carbonate and ammonium tetrafluoroborate furnished the corresponding allylic complexes (Scheme 19).

The NMR characterization showed that the three complexes were present as mixtures of isomers, due to the unsymmetrical nature of MaxPHOS (**L54**),[53,99] although the crystal structures contained only one isomer. The allylic complexes were used in enantioselective allylic substitution reactions, but the conversions and enantioselectivities were only moderate.[99]

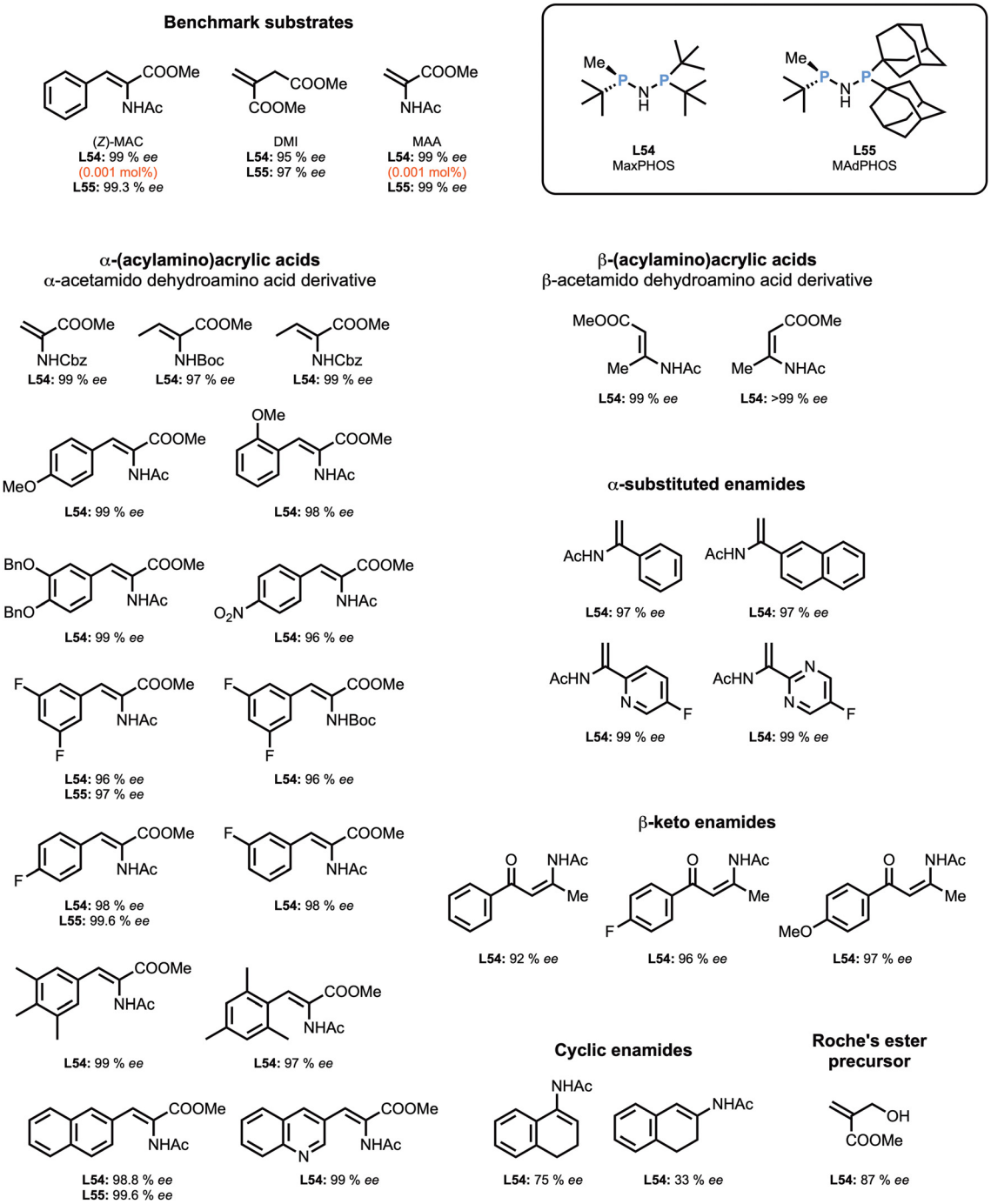
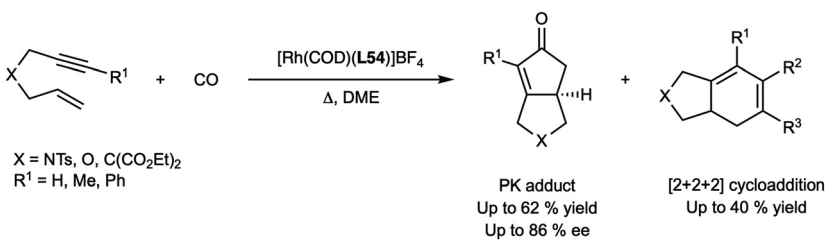
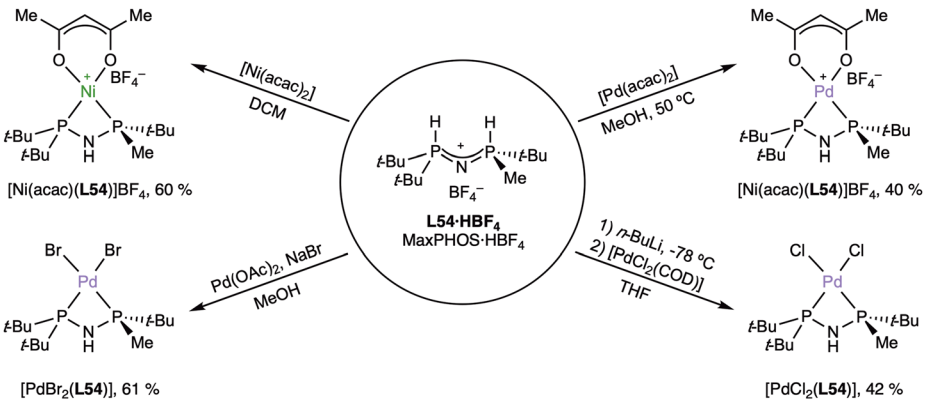


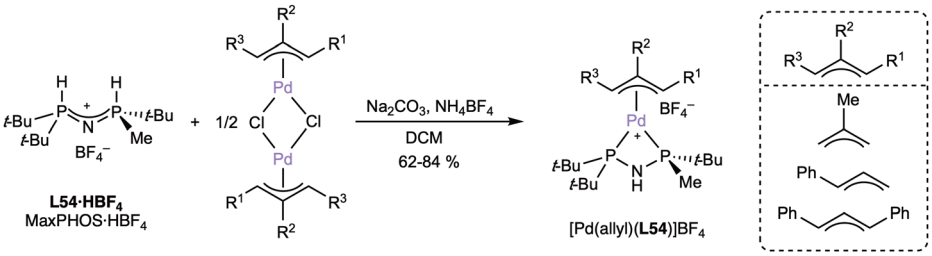
Fig. 11 Asymmetric hydrogenation with MaxPHOS (**L54**) and MAdPHOS (**L55**).



Scheme 17 Pauson-Khand reaction of enynes catalyzed by Rh-MaxPHOS (**L54**).



Scheme 18 Coordination compounds of Ni(II) and Pd(II) with MaxPHOS (**L54**).



Scheme 19 Preparation of palladium(II) allylic complexes with MaxPHOS (**L54**).

The increased stability of MAdPHOS (**L55**) compared to MaxPHOS (**L54**) made the same group explore the coordination chemistry towards Ni(0).[90] To this end, MAdPHOS (**L55**) was reacted with [Ni(cod)$_2$] (Scheme 20).

Using dichloromethane as a solvent, a mixture diastereomers for the bis(chelated) complexes was obtained, while in the case of using benzene, only the monochelated Ni-cod complex was obtained instead, although it was found to be rather unstable.

The coordination of MaxPHOS (**L54**) to organometallic octahedral moieties has also been explored by Ferrer, Carmona and Grabulosa,[100] with the preparation of rhodium(III), iridium (III) and ruthenium(II) complexes. Thus, the reaction of MaxPHOS·HBF$_4$ (**L54·HBF$_4$**) with [M(acac)ClCp*] (M = Rh, Ir) in refluxing dichloromethane produced the clean substitution of the acac ligand, giving the corresponding complexes in around 90% yields (Scheme 21).

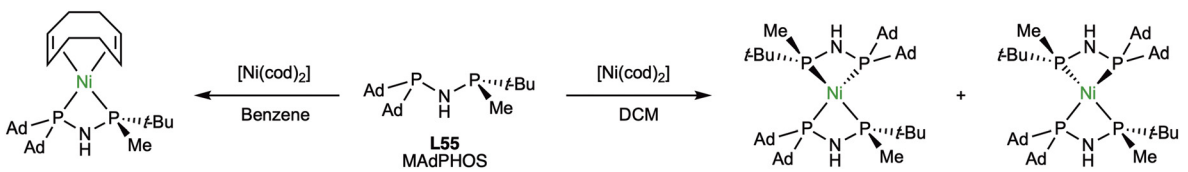
The characterization of the complexes demonstrated that they were present as a single species. It should be noted that the metal becomes a pseudotetrahedral, stereogenic centre so two different diastereomers, with different metal absolute configuration could be formed. The X-ray crystal structures demonstrated that both complexes had S_M configuration, starting from S_P-MaxPHOS·HBF$_4$ (**(S_P)-L54**), with a very small bite angle of 68.85° for both complexes.

The complexation to ruthenium(II) through the same method using an acac precursor[101] gave only traces of the product,[100] but the reaction was successful using the MaxPHOS ligand (**L54**), the typical ruthenium(II)-*p*-cymene dimer and ammonium tetrafluoroborate (Scheme 22).

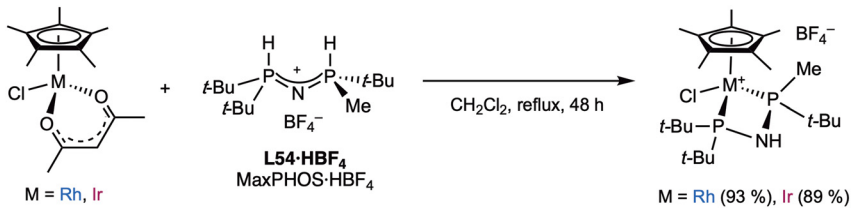
Again, the compound appeared as a single species and the crystal structure of the hexafluorophosphate salt showed that the absolute configuration of the ruthenium atom was S_{Ru}.

An interesting cyclometallation reaction was observed upon halide abstraction on iridium complex (Scheme 23).

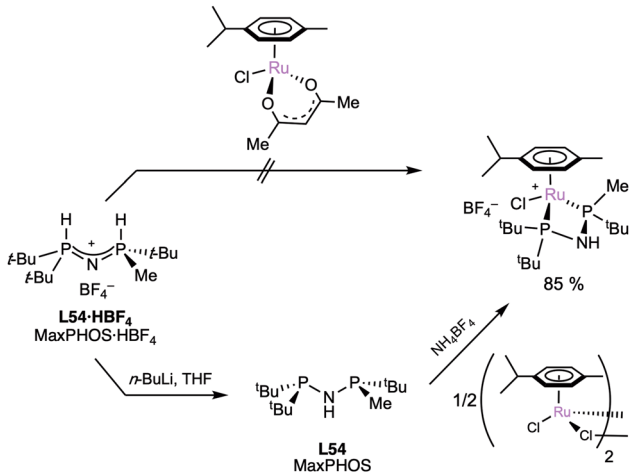
One of the *t*-butyl groups of the non-stereogenic phosphorus (P^2) in Scheme 23 cyclometallates *via* intramolecular C(sp^3)–H activation. Upon this activation, a new stereogenic



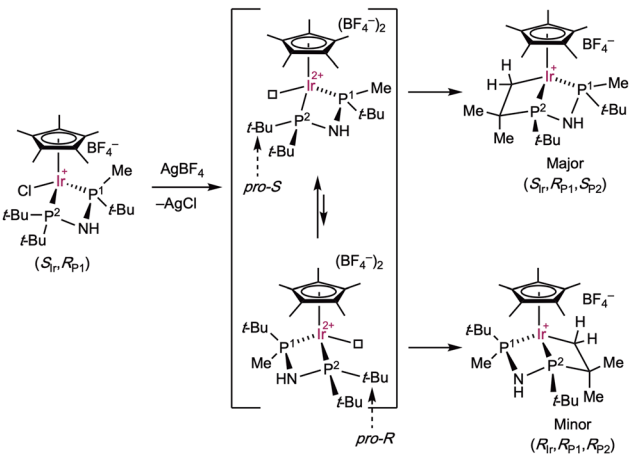
Scheme 20 Preparation of Ni(0)-MAdPHOS (**L55**) complexes.



Scheme 21 Reaction of (S_P)-MaxPHOS (**L54**) with [M(acac)ClCp*].



Scheme 22 Preparation of [RuCl(**L54**)(*p*-cymene)].



Scheme 23 C–H activation of *t*-butyl group on an iridium-**L54** complex.

centre in P^2 is created. NMR studies showed that two species, in 82 : 18 ratio, were formed and that they are those depicted in the scheme. A plausible mechanism for the formation of the two diastereomers is given in the scheme. Interestingly, this metalation was not observed when the analogous rhodium (Scheme 21) and ruthenium (Scheme 22) complexes were treated with silver tetrafluoroborate.

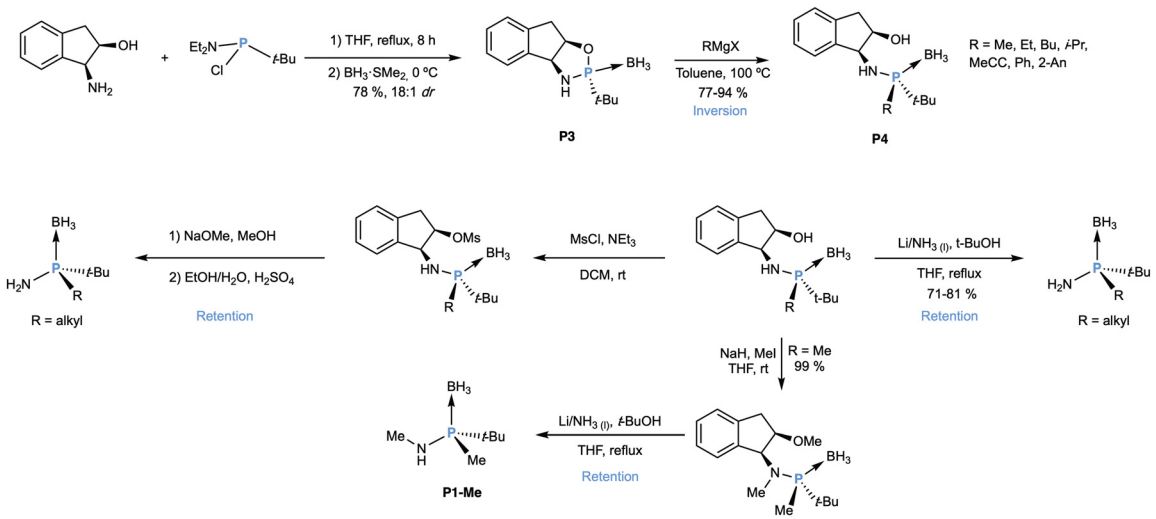
Although the method of Scheme 12 furnished **P1** as an enantiopure compound, it suffered from low yields due to the inefficient DKR and the relatively difficult synthesis of the racemic chlorophosphanes. Inspired by the oxazaphospholidine-based method of Jugé[41] the same group devised a strategy using another bifunctional, chiral auxiliary, *cis*-1-amino-2-indanol, both enantiomers of which are commercially available (Scheme 24).[102]

The condensation between (1*R*,2*S*)-*cis*-1-amino-2-indanol and racemic *t*-butylchlorodiethylaminophosphane, followed by boronation, produced the oxazaphospholidine-borane **P3** in good yields and high diastereoselectivity after a single recrystallization. This compound was susceptible to nucleophilic attack by carbanionic reagents and in this case Grignard reagents gave cleaner reaction than organolithiums at 100 °C in toluene, giving good yields of the opened aminophosphane-boranes, **P4**. Interestingly, X-ray crystallography showed that the opening reaction take place with *inversion* of configuration at the phosphorus atom, in contrast to the Jugé-Stephan methodology.[41] The origin of this difference was studied computationally[103] and it could be traced back to the substitution state of the nitrogen atom in oxazaphospholidine-boranes. In the case of 2-phenyloxazaphospholidines with the methylated nitrogen (Jugé-Stephan method[41]), the reaction takes place with retention of configuration by a two-step frontside $S_N2@P$ substitution, with in the case of an unsubstituted nitrogen atom, takes place with inversion of configuration by a single-step backside $S_N2@P$ substitution.

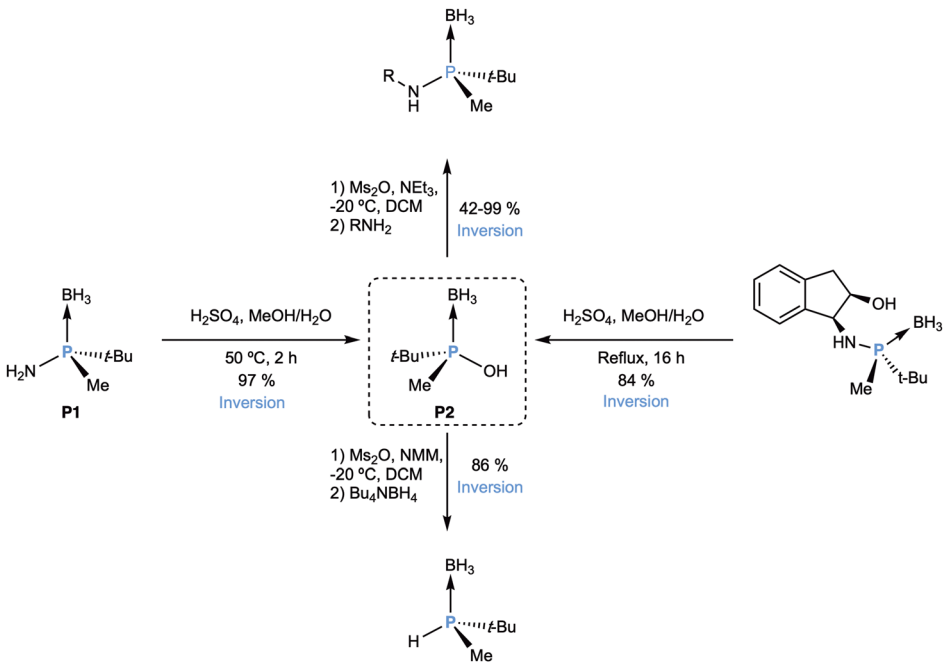
The desired primary aminophosphane-boranes with alkyl substituents could be easily obtained by reductive C–N cleavage of the chiral auxiliary. The *N*-methylated compound **P1-Me** could be also obtained by permethylation of the precursor and reductive cleavage.

The Li-mediated reduction of the C–N bond could not be applied to substrates with R = aryl, due to the formation of reduced, Birch-type products. Therefore, an acidic cleavage method on the mesylates was developed, furnishing the desired aminophosphane-boranes.

Aminophosphane-boranes, apart from being useful for the preparation of PNP ligands such as MaxPHOS (**L54**) and MAdPHOS (**L55**), are important synthons in *P*-stereogenic chemistry that can give other intermediates in the synthesis of other single-atom-bridged ligands (Scheme 25). The hydrolysis of either **P1** or, more conveniently, the aminophosphane-borane with the indanol group, could be carried out under rather forcing acidic conditions,[104] furnishing the phosphinous acid-borane **P2** as an optically pure compound. This com-



Scheme 24 Synthesis of aminophosphane-boranes by cleavage of the chiral auxiliary.



Scheme 25 Synthesis and reactivity of phosphinous acid-borane **P2**.

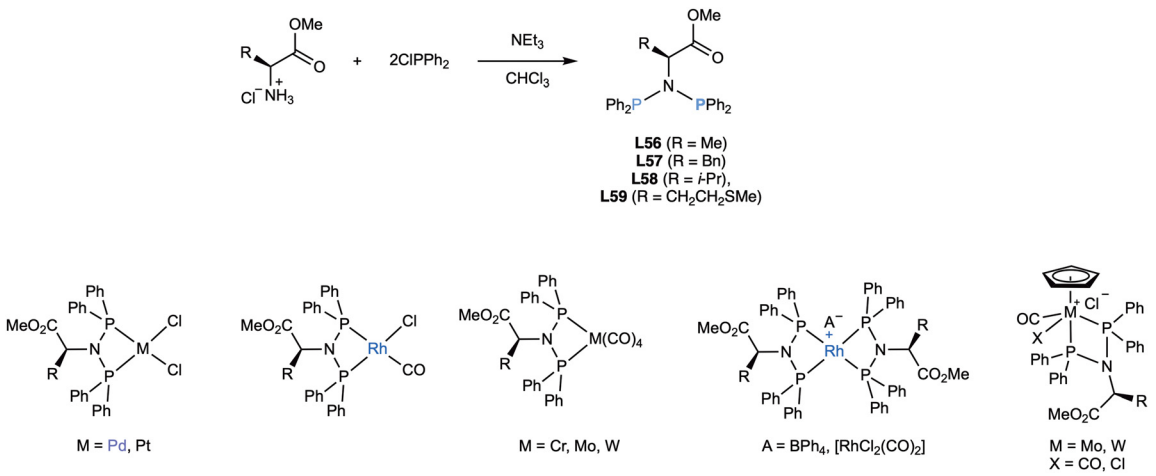
pound was a low-melting point semisolid that presented limited stability, but the same group devised a strategy to stabilize it as a dialkylammonium salt.[105]

This compound furnishes a secondary phosphane oxide (SPO) upon deboronation, whose coordination chemistry has been studied.[106] In addition, the hydroxyl could be activated by mesylation and the mesylate was a good leaving group in S_N2@P reaction by amines, with inversion of configuration. Interestingly, the S_N2@P reaction with tetrabutylammonium borohydride was also successful,[107,108] giving the important secondary phosphane-borane adduct HP(*t*-Bu)Me, which has been extensively used by Imamoto[14,109] in the synthesis of *P*-stereogenic ligands.

Substituted nitrogen bridge

As early as 1978, Beck[110] reported the synthesis of series of chiral diphosphazanes by reaction of chlorodiphenylphosphane with optically pure amino acids and obtained a surprising variety of ligands which demonstrated their tendency to coordinate in a bidentate fashion (Scheme 26).

The ligands were easily obtained by phosphination of natural amino acids (glycine, alanine, phenylalanine, methion-



Scheme 26 Early synthesis of chiral diphosphazanes (**L56–L59**) employing natural amino acids and some of their derived complexes.

ine) in 50–70% yields. Their reaction to palladium(II), platinum(II), and rhodium(I) standard precursors produced mononuclear complexes, which were thoroughly characterized.[110] Some years later,[111] the same ligands were reacted with [MCp(CO)$_3$Cl] (M = Mo, W), producing complexes (X = CO), which led to metal-stereogenic complexes (X = Cl) by thermal or photochemical replacement of CO by chloride. The diastereomers could be separated in the case of the ligand derived from valine (**L58**). Many years later, Woollins and coworkers[112] also revisited the synthesis of **L56** (which they named bdppal) and prepared the same [MCl$_2$(**L56**)] complexes, which were analysed by X-ray diffraction. In addition, they prepared the mono- and dioxidised versions (with oxygen and sulphur) of **L56** and studied their coordination to palladium(II) and platinum(II).

In 1981, Payne prepared[113] two more diphosphazanes, **L60** (peap) and **L61** (alap) employing the same method and studied their complexation towards platinum (Fig. 12).[113,114]

The ligands were prepared in moderate yields from optically pure phenylethylamine and the ethyl ester of alanine and were reacted with [Pt(cod)ClMe] to give the neutral platinum(II) complexes, which were converted into the cationic complexes by halide abstraction in the presence of a monodentate ligand, namely acetone, a *p*-substituted pyridine or a monophosphane.[113] All this array of complexes was characterized in great detail by NMR with the aim of studying the electronic and steric properties of the ligands. In a parallel study,[114] the platinum(0) complex (Fig. 12, right) with peap (**L60**) and acetylene was prepared and its crystal structure determined. A few years later, Basset and coworkers[115] reported the use of (*S*)-peap (**L60**) to prepare the rhodium cluster [Rh$_6$(CO)$_{10}$(peap)$_3$], which was found to be inactive in the hydrogenation of dehydroaminoacids.

The ligand peap (**L60**), almost exclusively the *S* enantiomer, has been employed to prepare many complexes for several applications and the ligand itself has been used for NMR studies.[116–118] Most of the complexes reported so far contain the free peap (**L60**) and are given in Fig. 13, but there are others, not shown, with the ligand oxidized, forming a sulphide or a selenide.[119–123]

Square-planar complexes **C5–C7** were obtained by Krishnamurthy[28] with standard metallic precursors. The nickel complex **C4** was not obtained until much later by Hadjichristidis[124] by treating (*S*)-peap (**L60**) with [NiCl$_2$(PPh$_3$)$_2$], and has been more recently used to prepare maleonitriledithiolate complexes that act as electrocatalysts for hydrogen evolution.[125] A few years later, the corresponding dibromide complex was prepared from [NiBr$_2$(dme)].[126] The platinum dichloridocomplex (**C6**) was hydrolysed in wet acetone in the presence of silver triflate to give the bis(aqua) complex, which was used in hydration of alkynes in micellar media.[127] Interestingly, bis(chelated) complex **C7** was obtained with [Rh(cod)$_2$]BF$_4$ regardless of the ratio ligand : metal, demonstrating the marked tendency of peap (**L60**) to produce chelated complexes.[28] Slightly later Navarro,[128] also described **C5** and **C6** and observed that one of the P–N bonds of was cleaved when the complexes were treated with alcohols. The same group studied further the chemistry of **C5** and **C6**.[129] Treating them with silver perchlorate produced the dimers **C8** and **C9**, which reacted with thallium acetylacetonate to give the acac complexes **C10** and **C11**, respectively. Platinum complex **C9** was reacted with α-amino acids L- and D-alanine, giving α-amino acidato complexes **C12**. When racemic alanine was used, no discrimination was observed in the formation of **C11**. The reaction of **C6** with diazomethane furnished bis(chloromethyl) complex **C13** but, in contrast, the reaction with ethyl diazoacetate resulted only in the insertion to only one of the Pt–Cl bonds, giving a mixture of two diastereomers due to the formation of a stereogenic carbon atom in **C14**.

Krishnamurhthy[130] reacted (*S*)-peap (**L60**) with [RuCpCl(PPh$_3$)$_2$] in toluene at 100 °C and found that a mixture of neutral complex **C15** and cationic complex **C16** formed and isolated them in 80 and 5% yields respectively. At the same time, Gamasa[131] prepared series or indenylruthenium(II) complexes. The starting complex **C17** was prepared from [RuCl

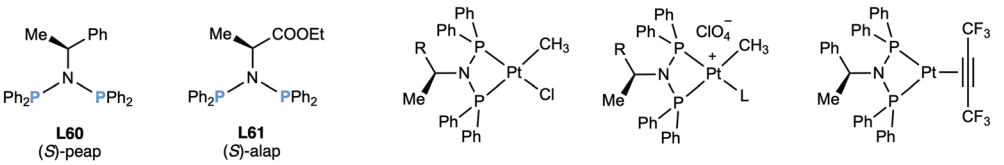


Fig. 12 The diphosphazanes peap (**L60**) and alap (**L61**) and their first described complexes.

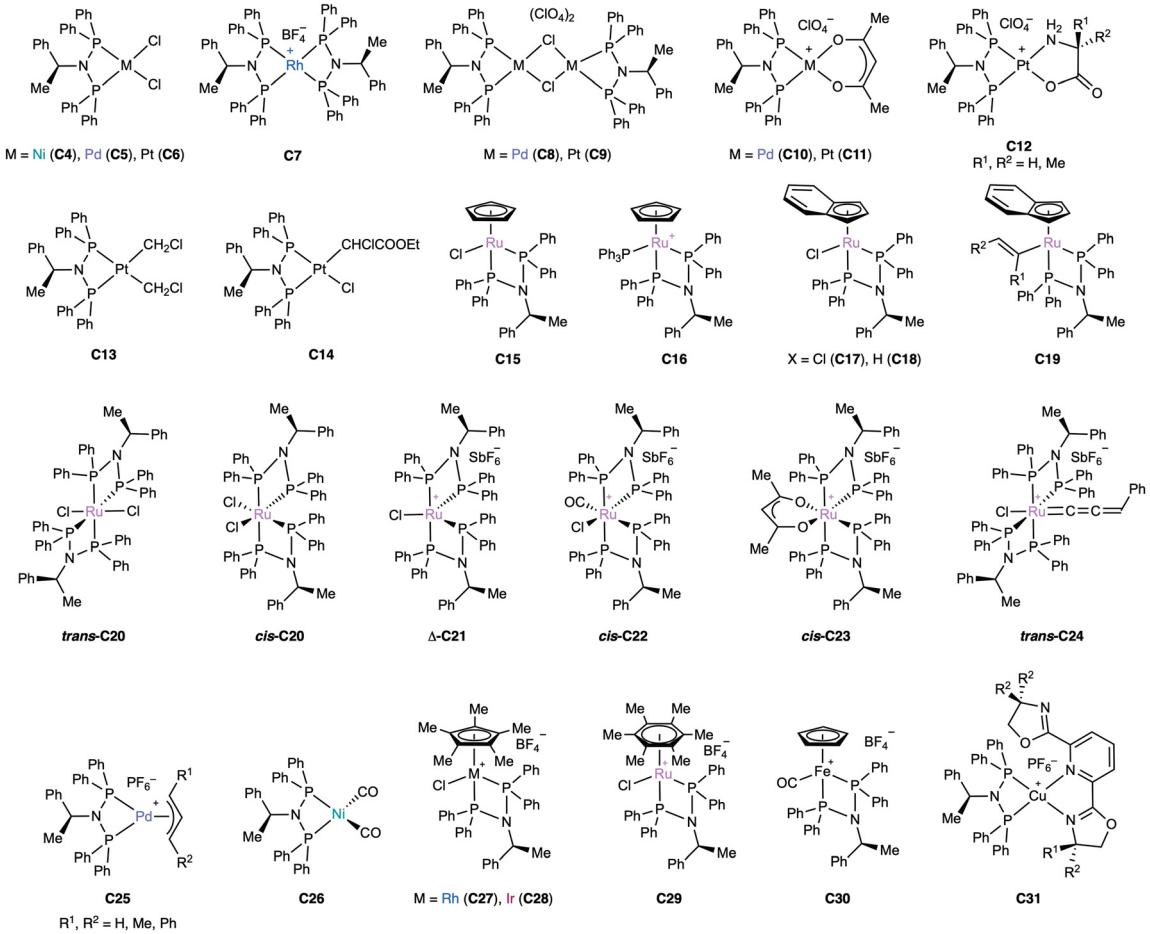


Fig. 13 Most of the described complexes with the peap ligand (**L60**).

(indenyl)(PPh_3)$_2$] in toluene at reflux. This complex was converted into the hydride **C18** in 85% yield by treatment with sodium methoxide in methanol. This method exploits the by β-hydrogen elimination of the methoxy complex formed *in situ*. Complex **C18** was characterized by X-ray diffraction. This complex was reacted with alkynes providing several alkenyl complexes **C19**, some of which were converted to ruthenium carbenes (alkenylalkylidenes) by protonation with tetrafluoroboric acid. Their catalytic activity in ring closing metathesis of diethyldiallylmalonate was investigated but they were found to be inactive. Further work of the same group[132] focused on five- and six-coordinated ruthenium(II) compounds. Treatment of [$RuCl_2$(dmso)$_4$] with (*S*)-peap (**L60**) stereoselectively produced ***trans*-C20**, which could be photochemically isomerized to the less stable ***cis*-C20**. Halide abstraction of ***trans*-C20** with silver hexafluoroantimonate gave the cationic, five-coordinated, 16-electron complex **Δ-C21**, which was characterized by X-ray diffraction and was present as a single stereoisomer. This complex was a good intermediate to other complexes and hence carbonyl complex ***cis*-C22** was selectively produced, which slowly isomerized to the *trans* isomer. The acac complex ***cis*-23** was also prepared. Finally, reaction of **Δ-C21** with 1-phenyl-2-propyn-1-ol afforded the allenylidene derivative ***trans*-C24**.

Krishnamurhthy[122] described the complexation of (*S*)-peap (**L60**) to allylpalladium moieties and studied in detail, by NMR, the dynamics of complexes **C25** in solution. They found that when the allyl group was symmetrical (R^1 = R^2 in **C25**,

Fig. 13) the complexes existed as a single species in solution, in the case of unsymmetrical allyl moieties ($R^1 \neq R^2$ in **C25**, Fig. 13), an equimolar mixture of diastereomers was observed. The palladium-catalysed catalytic allylic alkylation of (*E*)-1-phenyl-2-propenyl acetate was investigated and while good conversions were found, the regioselectivity was 96 : 4 favouring the achiral (linear) product.[122]

Valderrama[133] expanded the range of organometallic compounds by the preparation of nickel(0) complex **C26** from (*S*)-peap (**L60**) and nickel tetracarbonyl and piano-stool complexes **C27–C29** by reaction of the ligand with typical organometallic precursors. In addition, the interesting iron(II) complex **C30** was prepared from $[FeCp(CO)_2I]$ and silver tetrafluoroborate. Several crystal structures were obtained.

There is an interesting example of copper(I) complex (**C31**) containing a pybox ligand reported by Gamasa.[134] It was prepared from a dimeric precursor, and it was found to be stable in air.

These early-prepared ligands (Fig. 12) remained the sole examples of enantiopure diphosphazanes in the literature for quite some time. The outlook of the 1994 excellent review of Krishnamurthy and coworkers[78] when referring to the coordination chemistry of (mainly achiral) diphosphinoamines affirmed that "*it would also be interesting to incorporate chiral entities into acyclic diphosphazane ligands and use such chiral diphosphinoamines to synthesize transition metal complexes that may function as homogeneous catalysts*". This statement proved to be true in no small part due to the work of his own group in the subsequent years.

In 1995 a first article on the preparation of diphosphazanes derived from (*S*)-methylbenzylamine appeared (Scheme 27).[28]

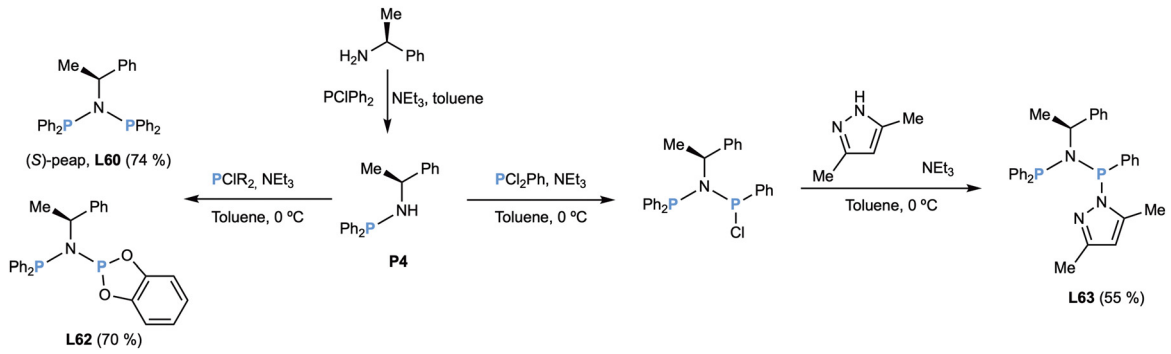
The key optically pure aminophosphane **P4** was easily prepared by condensation of methylbenzylamine and chlorodiphenylphosphane. The nitrogen was phosphinated again with a chlorophosphane to give the known ligand peap (**L60**) and the new ligand **L62** in good yields. Interestingly, the reaction with dichlorophenylphosphane gave a chlorinated intermediate with a stereogenic phosphorus atom, with a small chiral induction. The derivatization with dimethylpyrazole furnished ligand **L63** in moderate combined yield of the two diastereomers. Pleasingly, the two diastereomers could be separated by fractional crystallization.[28]

There has been some organometallic chemistry, carried out by the same group, with ligand **L63**. In the first report,[135] it was used to obtain a rather unusual heptacoordinated molybdenum complex $[Mo(\kappa^3\text{-}N,P,P\text{-}\mathbf{L63})(CO)_2I_2]$, in which the ligand coordinates through both phosphorus atoms and the pyrazolic nitrogen. Much later, the same ligand was employed to prepare and study the structure and dynamics of allylpalladium complexes $[Pd(\eta^3\text{-}C_3H_4R)(\mathbf{L63})]PF_6$ (R = Me (crotyl), Ph (cinnamyl)).[136] Interestingly, the ligands coordinated in *N*,*P* fashion instead of the expected *P*,*P* fashion. In contrast, with the monosulphide of **L63** (in the non stereogenic phosphorus), the *P*,*S* coordination was observed. A follow-up study was published, in which the allylic complexes with 1,3-dimethylallyl and 1,3-diphenylallyl were also prepared and studied.[137] Interestingly, in the case of the later allyl group, a mixture of *N*,*P* and *P*,*P* coordinations was found. The ligand was used in the catalytic allylic alkylation of the model substrate *rac*-1,3-diphenyl-2-propenyl acetate, but despite full conversion being achieved, only 30% ee was observed.[137]

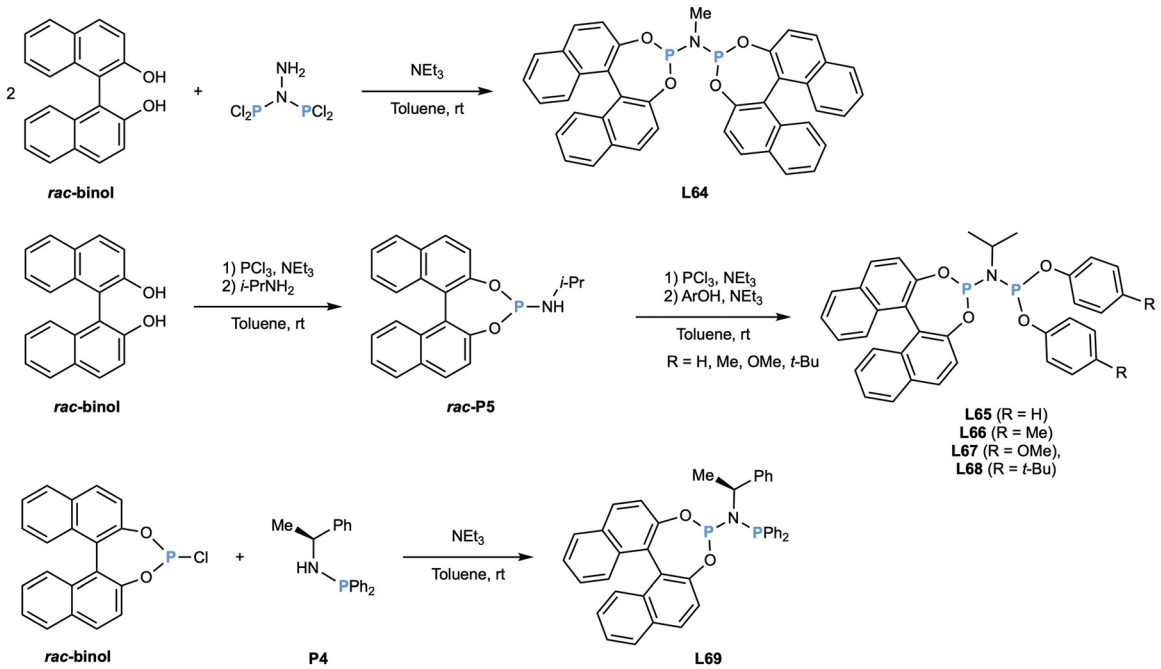
At the same time,[130,138] optically pure $(\boldsymbol{S_C,R_P})$**-L63** was coordinated to ruthenium(II) and the neutral complex $[RuCpCl(\kappa^2\text{-}P,P\text{-}\mathbf{L63})]$ could be isolated in a diastereomerically pure form as the isomer with R_{Ru} configuration at the ruthenium atom according to the X-ray crystal structure.[130] Many other ruthenium-Cp complexes with achiral ligands were described in the same report.[138] There is also a report[139] in which the ligand was reacted with $[Ru_3(CO)_{12}]$ to furnish a phosphido cluster by cleavage of the $P\text{–}N_{pyrazole}$ bond, with the pyrazolate moiety adopting an unusual triply bonding $\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1$ coordination mode.

The same group,[130,140,141] applying methods previously developed to prepare achiral or racemic unsymmetrical diphosphazanes[142,143] prepared ligands introducing the typical 2,2-binaphthol moiety (Scheme 28).

They mainly used racemic binol, although they mentioned that the ligands could also be prepared starting from the optically pure binaphthol and they prepared them in optically pure form in a subsequent study.[144] The synthesis of the ligands



Scheme 27 Preparation of chiral diphosphazanes **L60** (peap), **L62** and **L63**.

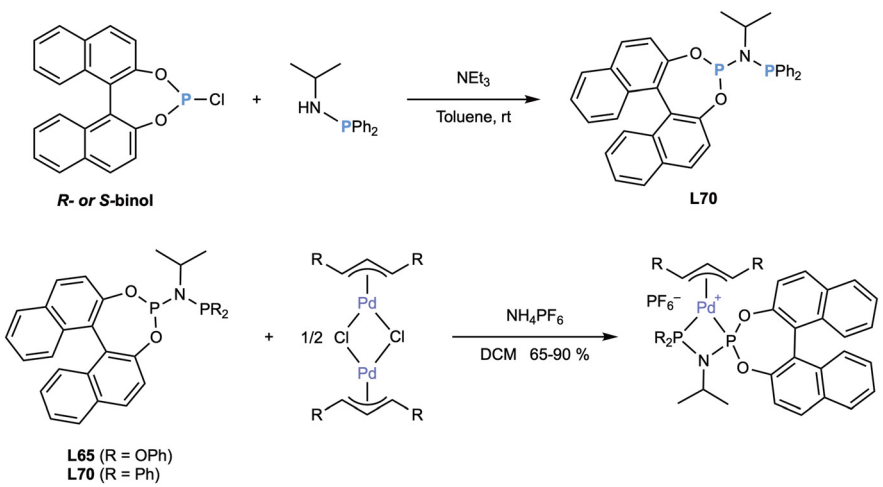


Scheme 28 Preparation of diphosphazanes with the racemic binaphthol moiety.[130] The same group had published achiral or racemic ligands before.[143]

were based on classic condensations between P–Cl and O–H moieties in the presence of triethylamine and gave ligand **L64** with bis(dichlorophosphino)methylamine, whose diastereomers (*meso* and *rac*) could not be separated. For the preparation of unsymmetrical diphosphazanes, a multistep synthesis, always based on condensations, was devised and gave ligands **L65–L68**. Interestingly, with the aim of obtaining an enantiopure ligand, diphosphazane **L69** with the optically pure group in the bridge was prepared as a mixture of diastereomers, but they could not be separated by fractional recrystallization and the same happened with the monosulphide. The separation was finally possible from the palladium complex [$PdCl_2$(**L69**)]. Finally, some ruthenium-cyclopentadienyl complexes with the achiral or racemic ligands were also prepared[130] and used to prepare ruthenium carbonyl clusters by reaction with [$Ru_3(CO)_{12}$].[144]

The same group a few years later described the synthesis of the enantiopure versions of ligand **L65** (Scheme 28) and described the synthesis of another enantiopure ligand (**L70**), which had been described before[143] as a racemate (Scheme 29).[141]

The allylpalladium complexes were prepared with the racemic ligands and their structures were studied by NMR and X-ray structural analysis. The enantiopure ligands were used in



Scheme 29 Preparation of diphosphazane **L70** with complexation to allylpalladium moieties.

the catalytic allylic alkylation of the model substrate *rac*-1,3-diphenyl-2-propenyl acetate with dimethyl malonate and *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (Scheme 30).

Full conversion was observed after 24 h, but only 20–44% ee values were obtained.[141]

Slightly later, a comprehensive study of the complexation of many achiral diphosphazane ligands, but also enantiopure (*S*)-peap (**L60**) to form half-sandwich (Cp and Cp*) ruthenium(II) complexes was published by the same group.[145] The unsymmetrically-substituted diphosphazanes gave complexes with stereogenic ruthenium atoms. In the case of binaphthyl-containing diphosphazanes, it was the binaphthyl moiety that controlled the stereochemistry of the ruthenium atom. The chlorido complexes could be converted into the hydride complexes by treatment with sodium methoxide in methanol and this reaction proceeded stereoselectively if the substituents of the phosphorus were sterically bulky. Finally, they also used several of the enantiopure ligands developed in their group to study the catalytic enantioselective transfer hydrogenation of 2-acetonaphthone (Scheme 31). They found in generally good yields after 16 h, but with low enantioselectivities (<35% ee).

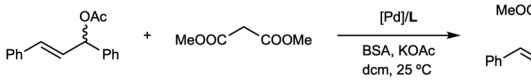
In 2004, Faraone and coworkers[61] reported a few new PNP ligands with a substituted nitrogen bridge with several stereogenic elements to study their combined effect in coordination chemistry and catalysis (Fig. 14).

The bis(diphosphino)alkylamine **L71** and the bis(diphosphonito)alkylamines **L72** and **L73** were obtained in good yields by the condensation of the primary amines and diphenylchlorophosphane or binaphthyl-phosphorochloridite in toluene in the presence of triethylamine. The presence of conformers was detected by NMR due to restricted rotation around the P–N bonds.[61] The interesting "mixed" phosphino-phosphonitoamine ligand **L74** was obtained in 45% yield taking advantage of the different rate of hydrogen substitution from *s*-butylamine.[28]

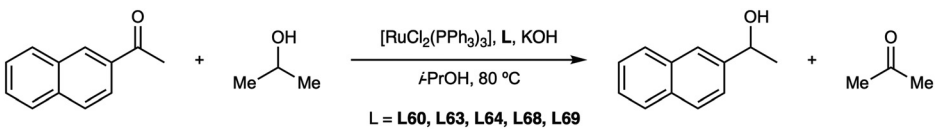
The ligands were developed for palladium-catalysed allylic alkylation and therefore the synthesis of allylpalladium complexes was studied. It was found that in all cases the standard, mononuclear complexes with typical bidentate coordination of the ligands [Pd(η^3-1,3-diphenylallyl)(P–N–P)]X (X = PF_6 or OTF) were formed. Detailed NMR experiments to study the number and identity of the different species and their interconversion were carried out. Finally, the application of the ligands in enantioselective allylic alkylation of model substrate 1,3-diphenylallyl acetate with dimethyl malonate and BSA and potassium acetate was studied. Symmetric ligands **L71–L73** gave a racemic alkylation product while non-symmetric (phosphino-phosphonito)amine gave the product with only 18% ee.

In a parallel publication, the same group[146] studied the coordination of **L71**, **L72** and **L74** to other palladium(II) moieties to platinum(II) and rhodium(I) precursors. Starting from typical precursors, they were able to obtain the coordination compounds [M(**L76**)Cl_2] (M = Pd, Pt), [Rh(**L71**)(cod)]PF_6 and [M(**L**)X_2] (M = Pd, Pt; **L** = **L72**, **L74**; X = Cl, I). The crystal structure of palladium and platinum complexes with **L71** showed that they were isostructural with very similar geometrical parameters. Ligands **L73** and **L74** and [Rh(acac)$(CO)_2$] were used in hydroformylation of styrene but no hydroformylation products were observed.

The group of Riera and Verdaguer also reported a few years later a different type of ligands, named ThaxPHOS (**L75–L79**), easily prepared from oxazaphospholidine **P3** (Scheme 24) by



Scheme 30 Palladium-catalysed allylic alkylation of *rac*-1,3-diphenyl-2-propenyl acetate.



Scheme 31 Ruthenium-catalyzed transfer hydrogenation of 2-acetonaphthone.

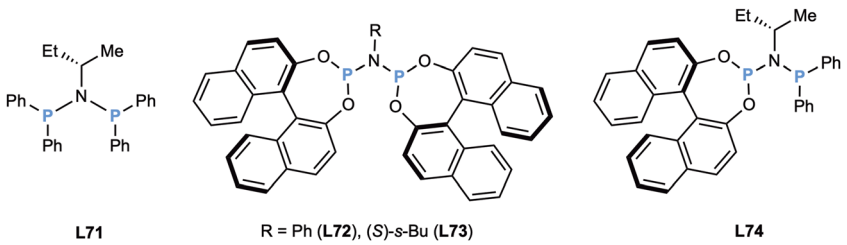
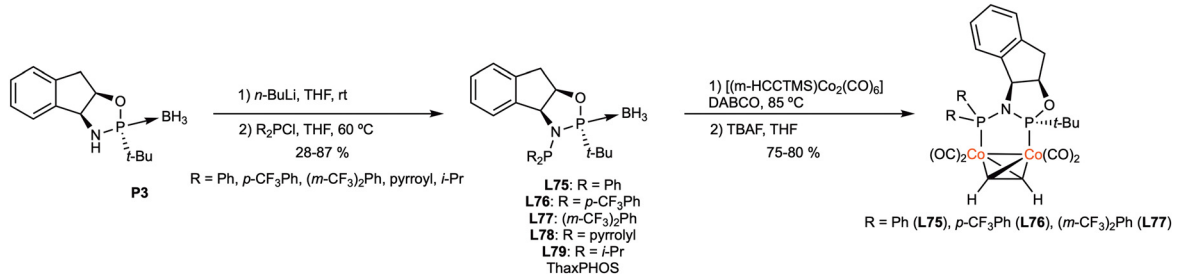
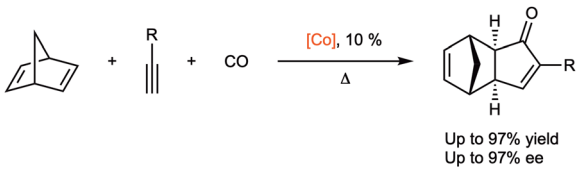


Fig. 14 PNP ligands prepared by Faraone and coworkers.[61]



Scheme 32 Synthesis of the ThaxPHOS ligands (**L75–L79**) and complexation to Co-acetylene moieties.



Scheme 33 Intermolecular PK catalyzed by Co-ThaxPHOS (**L75–L77**).

deprotonation and phosphination of the NH group (Scheme 32).[147]

The ligands were obtained as pure compounds by a simple recrystallization without need to protect the second phosphorus moiety. The deprotection with DABCO and reaction with a cobalt precursor, followed by desilylation with tetrabutylammonium fluoride (TBAF) produced the cobalt-acetylene complexes shown in the scheme as single species, with an "A-frame" structure, as confirmed by X-ray diffraction. These complexes were used in intermolecular enantioselective Pauson-Khand (PK) reactions at 1 bar of carbon monoxide (Scheme 33).[147]

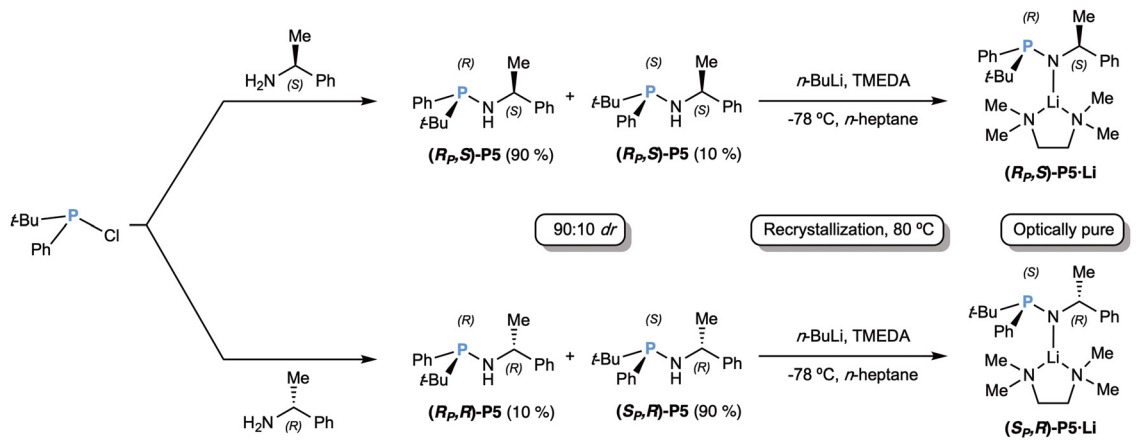
The complexes were active in intermolecular PK reactions of several alkynes and norbornadiene, giving the corresponding *exo*-cyclopentenones. The best alkyne, in terms of enantioselectivity was trimethylsilylacetylene. These results compare very favourably to those obtained much earlier by Gimbert with peap (**L60**) and other electron-deficient diphosphazane ligands.[148]

More recently, Kamer and coworkers[30,149,150] reported in three consecutive articles, a clever strategy to obtain a group of *P*-stereogenic diphosphazanes containing other stereogenic elements, collectively abbreviated as JoSoPhos.[30]

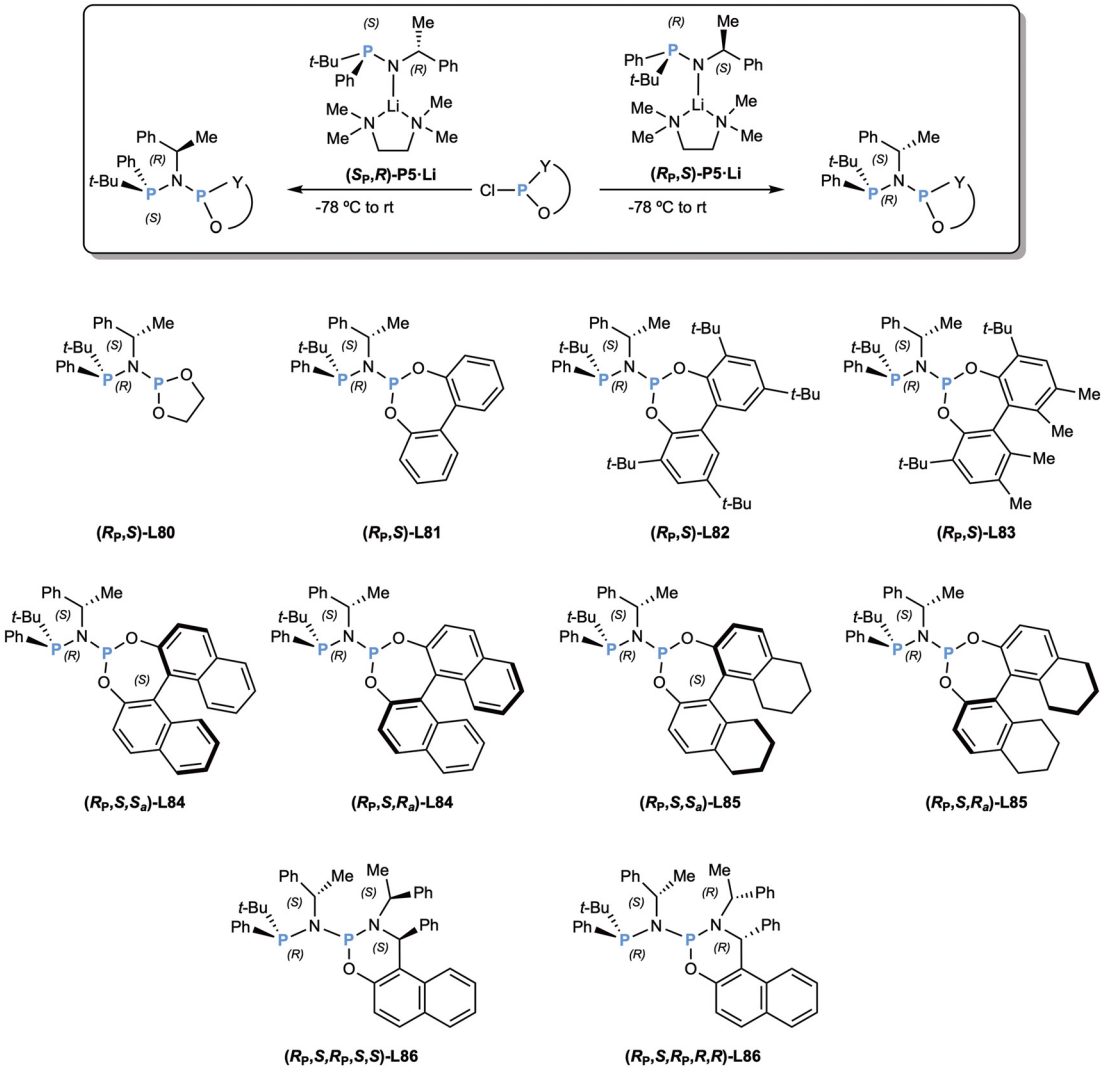
The synthesis started by reproducing earlier work of Kolodyazhnyi,[151,152] by preparing phosphanamine **P5** in high yield as a 90 : 10 mixture of diastereomers, using racemic *t*-butylchlorophenylphosphane and each enantiomer of 1-phenylethylamine (Scheme 34, compare with Scheme 12).[30,149]

The diastereomeric mixtures of **P5** were deprotonated with *n*-BuLi/TMEDA, producing lithium phosphinoamides **P5·Li** as a solid in the same diastereomeric ratios but upon recrystallization at 80 °C in *n*-heptane, they could be obtained as a diastereomerically pure solids, **(R_P,*S*)-P5·Li** or **(S_P,*R*)-P5·Li**.

This salt is an excellent synthon with a nucleophilic nitrogen, ideally suited to obtain ligands by reaction with chlorophosphanes in moderate yields (Scheme 35).[30,149] Therefore, it was reacted at low temperature with 2-chloro-1,3,2-dioxaphospholane (ligand **L80**), with phosphorochloridites derived from bisphenols (ligands **L81–L83**) and those of derived optically pure BINOLS (ligands **L84** and **L85**). The stereogenic phosphorus was found to be stable unless it was heated above 80 °C.[153]



Scheme 34 Preparation of both enantiomers of nucleophilic synthon **P5·Li**.



Scheme 35 General procedure to obtain optically pure JoSoPhos (**L80**–**L86**) ligands starting from **1**·Li and chlorophosphanes (top) and the exact ligands prepared (bottom). For the sake of simplicity, only those ligands prepared from (*R*P,*S*)-P5·Li are displayed.

The same group expanded this methodology for the synthesis of *P*-stereogenic phosphane-diamidophosphite ligand **L86**, containing five stereogenic centres; two phosphorus and three carbons.[150] The required phosphoramidochloridites could be easily obtained by condensation of phosphorus trichloride and the Betti base,[154] easily obtainable from cheap reagents.[155] The absolute configuration of the phosphorus atoms could be deduced from multinuclear NMR and crystal structure analysis. The ligands were found to be stable under inert atmosphere, but their non-cyclic stereogenic phosphorus atoms were found to be configurationally unstable above 60 °C.

As the JoSoPhos ligands were developed for rhodium-catalyzed enantioselective hydrogenation, their coordination towards rhodium(I) moieties was studied by NMR.[30,149,150] Those studies showed that the reaction of (*R*P,*S*)-**L80** with [Rh(diene)$_2$]BF$_4$ produced the bischelated complex [Rh(**L80**)$_2$]BF$_4$ in solution as a major product according to ^{31}P NMR spectroscopy, regardless of the metal : ratio employed. On the other hand, bulkier ligand (*R*P,*S*,*S*a)-**L85** produced the expected monochelated complex [Rh(**L85**)(cod)]BF$_4$ or the bis(chelated) species [Rh(**L85**)$_2$]BF$_4$ depending on the used rhodium precursor : ligand ratio.[156] This kind of behaviour had been observed by Pizzano,[157] Vidal-Ferran[158] and Grabulosa[29] (Fig. 7) for other non-symmetric diphosphorus ligands. A crystal structure determination[149] of [Rh(**L80**)$_2$]BF$_4$ revealed that in the crystal the complex had the expected square-planar geometry around rhodium(I) and that the ligands were in mutual *trans* arrangement. The differences in coordination behaviour had an impact in hydrogenation, which was studied with a wide variety of substrates (Fig. 15).

The JoSoPhos ligand library demonstrated high catalytic performance in the enantioselective hydrogenation of several types of di- and trisubstituted enamides and other challenging olefins, with a wide functional group tolerance. In addition, the asymmetric synthesis of an anti-Parkinson drug (rasagi-

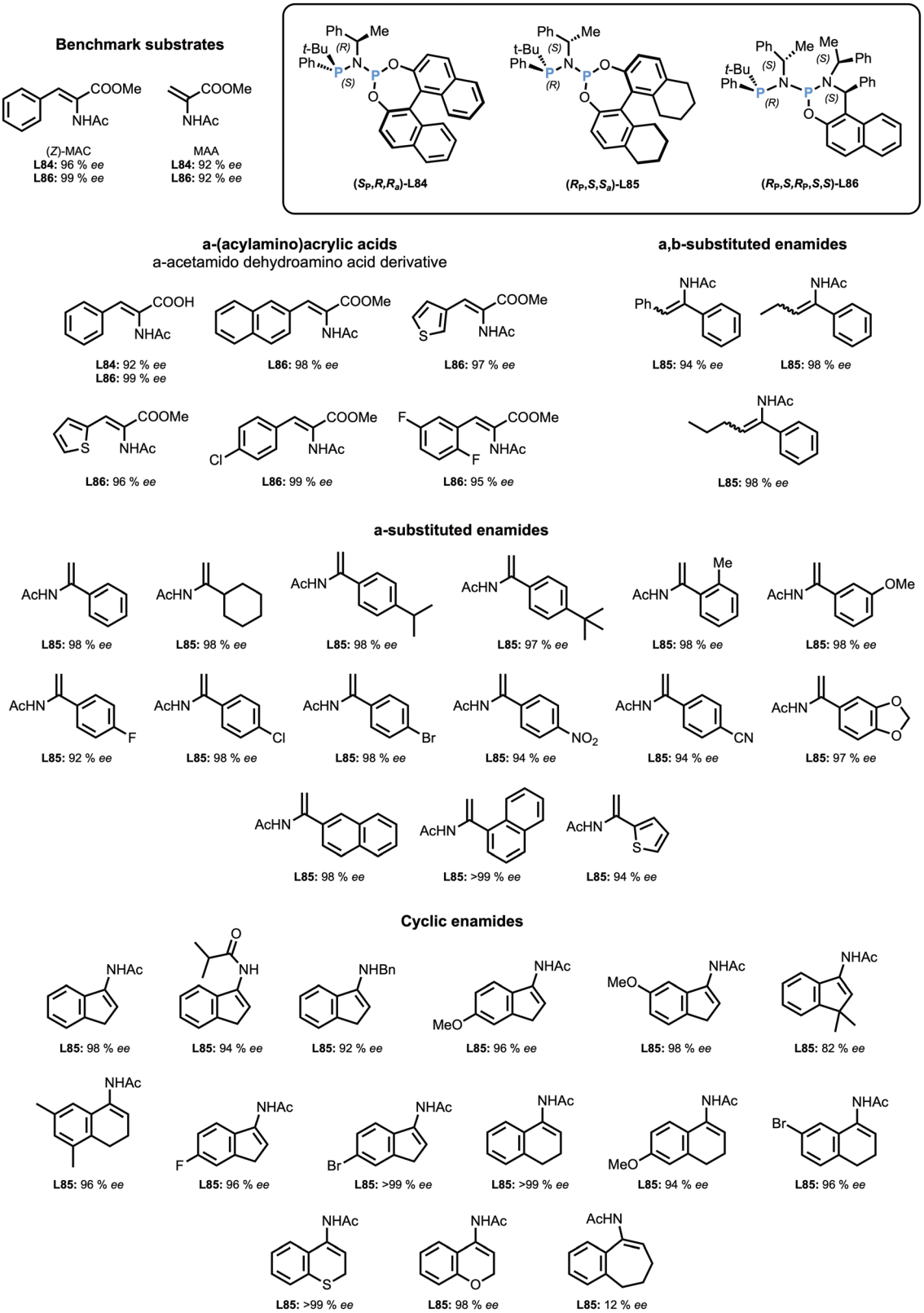


Fig. 15 Examples of asymmetric hydrogenation with JoSoPhos ligands **L84–L86**.

line) was presented, which had an enantioselective hydrogenation as a key step.[30]

O-bridged diphosphorus ligands (POP)

In the introduction it has been stated that scarcity of oxygen-bridged diphosphorus ligands (POP) is due to their tendency to suffer a phosphorotropic equilibrium between the bis(phosphorus(III)) tautomer (POP) and the phosphorus(II)–(III) tautomer PPO, favouring the latter, especially for electron-rich substituents (Scheme 2).[15] There are, however, cases in which the trivalent phosphorus tautomer can be stabilised.

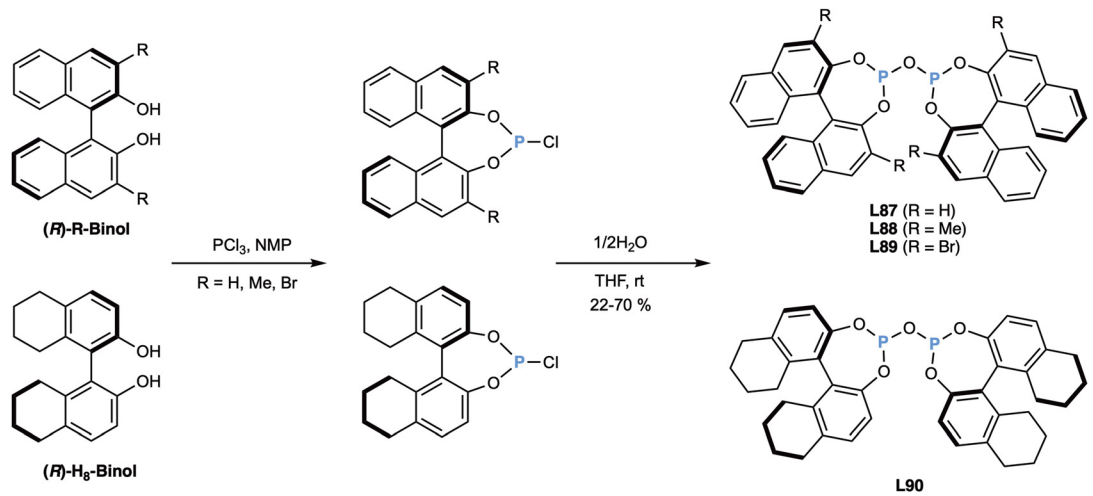
Pyrophosphites ($(RO)_2POP(OR)_2$) can be considered the analogues of the organic anhydrides of the carboxylic acids and it is known that the alkoxy substituents increase the stability of the POP form.[159] After a report on chiral (but racemic) pyrophosphites,[160] the first example of an enantiopure POP ligand did not appear until a 2003 in an article of Korostylev and Börner.[161] In this contribution, they prepared a small set of enantiopure pyrophosphites by simple two-step procedure (Scheme 36).

After the known preparation of the phosphorochloridites by the standard, solvent-free procedure in neat phosphorus trichloride, its controlled hydrolysis with a half equivalent of water gave the desired ligands **L87–L90** as crystalline, relatively stable solids. They used them *in situ* for enantioselective hydrogenations of model functionalized olefins (MAA and DMI) by treating the ligand with $[Rh(cod)_2]BF_4$. Quantitative yields were obtained and the enantioselectivities were only moderate in the best cases, which were achieved with H_8-binol derived ligand **L90** (48% ee for MAA and 70% ee for DMI). Investigations of the precatalyst solution showed the presence of many unidentified complexes, which were not isolated or further studied.

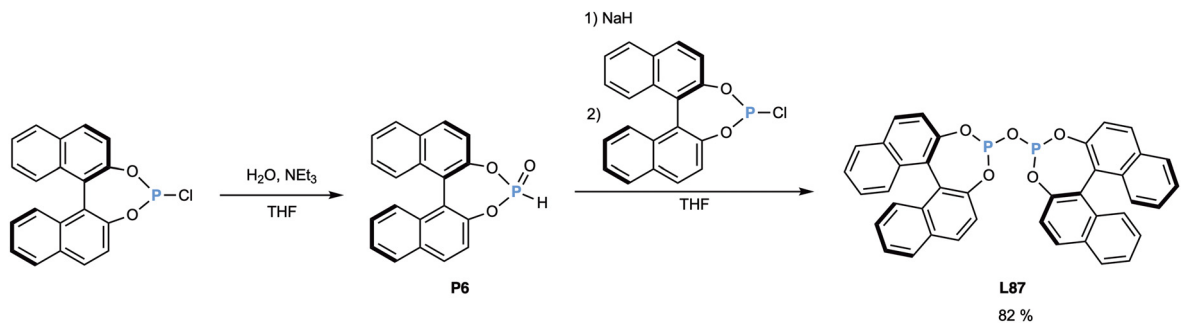
The following year, Faraone[61] reported the same ligand **L87**, obtained by a different synthetic method (Scheme 37).

The synthesis implied the complete hydrolysis of phosphorochloridite derived from binaphthol with water to give phosphonate **P6**, in tautomeric equilibrium with the corresponding phosphite,[16] which was deprotonated and reacted with another equivalent of the phosphorochloridite. The pyrophosphite **L87** was obtained in a high yield.

The coordination to palladium-η^3-allyl moieties furnished, according to detailed NMR experiments and conductivity,



Scheme 36 Preparation of enantiopure pyrophosphites based on binaphthol.



Scheme 37 Alternative preparation of pyrophosphite **L87**.

dimeric compounds $[Pd(\eta^3\text{-}1,3\text{-diphenylallyl})(\mathbf{L87})]_2(PF_6)_2$ in contrast to similar, PNP ligands (Fig. 14) which, as discussed before, form monomeric complexes. These dimers contain two palladium(II) centres bridged by two ligands and had been observed and characterised by Grabulosa with methylene-bridged diphosphanes (Fig. 7, complex E).[52] In the enantioselective allylic alkylation of 1,3-diphenylallyl acetate with dimethylmalonate, ligand **L87** provided the product in a 57% ee, which is much better than with the other ligands of Fig. 14, which is an interesting observation that has not been further explored in the literature.

Conclusions

The considerable corpus of work described in this perspective proves that chiral, single atom-bridged diphosphorus ligands PXP present a rich coordination and organometallic chemistry and have a high potential as ligands in enantioselective homogeneous catalysis. This was proved more than two decades ago by the superb activities and enantioselectivities obtained by the apparently very simple, methylene-bridged electron rich *P*-stereogenic PCP ligands described in the first part of the review. Clearly, the *P*-stereogenic moiety is a very powerful motif when forming rigid, four-membered chelate structures. More recently, equally good results have also been obtained with the analogous PNP ligands MaxPHOS (**L54**) and MAdPHOS (**L55**) with an unsubstituted nitrogen atom. In contrast, despite the large number of articles published, nitrogen-substituted PNP ligands have given much more modest results in catalysis up to now, with some exceptions, like the recently published JoSoPhos ligands (**L84–L86**). Despite this, due to their easy synthesis, this is certainly an area where new ligand design ideas could lead to discoveries of new efficient systems. Finally, the area of chiral POP ligands remains essentially unexplored, despite that it has been proven that pyrophosphites can be stabilized in their phosphorus(III) tautomers. Much more work is clearly needed to uncover the potential of PXP ligands in catalysis, but there is little doubt that the future will bring interesting new coordination chemistry and other exceptional ligands.

Data availability

No primary research results, software or code have been included. For analysis of crystal structures, crystallographic data from the CCDC has been used.

Conflicts of interest

The authors have no conflicts of interest to declare.

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