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Synthesis and application in asymmetric catalysis of P-stereogenic pincer–metal complexes

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P-stereogenic pincer–metal complexes are one of the most interesting pincer type organometallic compounds. Many kinds of this type of complexes were synthesized and used as catalysts in asymmetric catalysis. On the basis of our work in this field, this paper reports the recent progress in P-stereogenic pincer chemistry, including the synthesis of P-stereogenic pincer ligands, the synthesis of P-stereogenic pincer–metal complexes, and the achievements in P-stereogenic pincer–metal complex catalyzed asymmetric synthesis.

1. Introduction

As early as 1971, Nelson *et al.* reported a PNP type tridentate ligand 2,6-di(diphenylphosphinoethyl)pyridine and coordinated it with iron(II), cobalt(II), and nickel(II).[1] van Koten *et al.* then synthesized a NNN type tridentate ligand and proposed the concept of "pincerlike" to describe it in 1986.[2] Since then, with the development of the application of such complexes in metal catalysis,[3] pincer chemistry has gradually become a research hotspot in organometallic chemistry. Among these, the chiral pincer[4] is particularly remarkable.

Chiral pincer ligands can be divided into four types according to the different positions of chiral centers in the ligand (Fig. 1). (1) Substituents as chiral centers on the pincer skeleton.[5] Among them, the binuclear pincer–palladium complexes reported by Swager *et al.* are representative.[5i] (2) Substituents as auxiliary chiral centers on the coordination atom,[6] such as the chiral palladium bis(phosphite) pincer complexes reported by Pringle *et al.*[7] (3) Substituents as chiral centers at the benzylic position.[8] The PCP type pincer–Pd complexes developed by X. Zhang *et al.* are typical representatives of this kind of chiral pincer.[9] (4) P-stereogenic chiral pincer, like the PCP type pincer–Ni complexes reported by Wanbin Zhang *et al.*[10] This paper will focus on the P-stereogenic chiral pincer complexes.

The classical P-stereogenic pincer complex is a compound with four different substituents on the phosphorus atoms (Fig. 2, left). The substituents on phosphorus include methyl (Me), isopropyl (^{i}Pr), tertiary butyl (^{t}Bu), cyclohexyl (Cy), phenyl (Ph), and *ortho*-anisyl (*o*-An). In addition, there is a class of non-classical[11] P-stereogenic pincer complexes: the two heteroatoms (N or O) which bond to the pincer's phosphorus atoms are joined by chiral carbon chains to form heterocyclics (Fig. 2, right). In this paper, we will summarize

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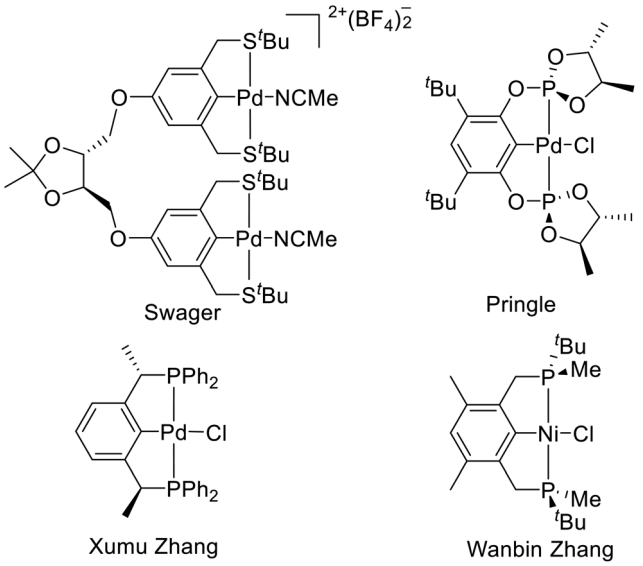

Fig. 1 Represent complexes of four type chiral pincers.

the recent progress of synthesis and application in asymmetric catalysis of both classical and non-classical P-stereogenic chiral pincer complexes.

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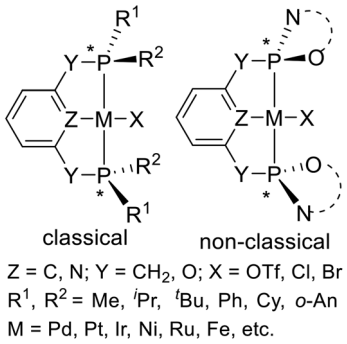

Fig. 2 The P-stereogenic pincer–metal complexes.

2. Synthesis of P-stereogenic pincer ligands

2.1 Synthesis of the classical P-stereogenic pincer ligands

2.1.1 Condensation of P-stereogenic synthons and halohydrocarbons. The basic procedure to produce pincer type P-stereogenic ligands is based on the synthesis of P-stereogenic synthons, that have been well summarized by Mezzetti *et al.*[12] It includes three pathways: ephedrine derived 1,2,3-oxazaphospholidine boranes,[13] enantioselective deprotonation with sparteine,[14] and menthyl phosphinates.[15] After obtaining the P-stereogenic synthons, the most common method to synthesize the classical P-stereogenic pincer ligands is by condensation of P-stereogenic synthons and halohydrocarbons.

Pioneering work was reported by X. Zhang *et al.*[16] Deprotonation of chiral synthon **1** with *sec*-BuLi *in situ* generates anion **2** (Scheme 1), which reacts with 2,6-bis(bromomethyl)pyridine **3a** or the 2,6-bis(bromomethyl)benzene **3b** to form **4a** and **4b** in high yields, respectively. After removing the borane groups from **4a** and **4b**, ligand **5a** and **5b** are obtained in pure form. This is a classical strategy to synthesize the classical P-stereogenic pincer ligands.

Following, many P-stereogenic pincer ligands were synthesized by this method (Fig. 3), such as the PNP^{tBu,Ph} (**6**) type pincer ligand reported by Livinghouse[17] and Castillón,[18] the PCP^{tBu,Ph} (**7**) and the PCP^{iPr,Ph} (**8**) type pincer ligands reported by

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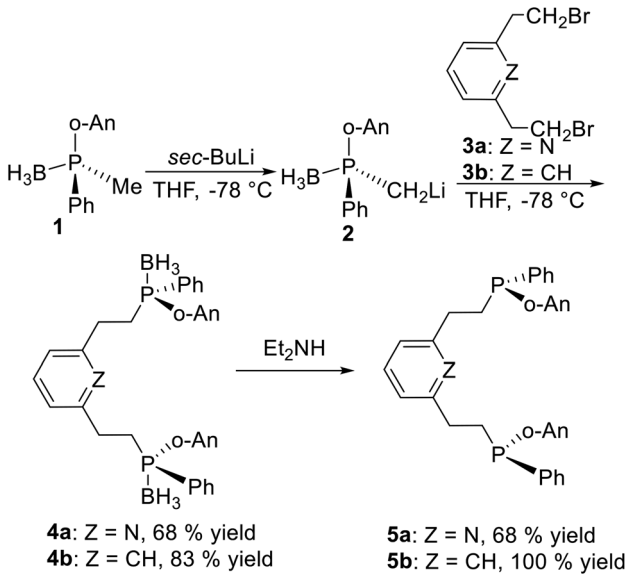


Scheme 1 Synthesis of P-stereogenic pincer ligands.

van Koten[19] and Morales-Morales,[20] the PCP^{tBu,Me} (**9**) and the PNP^{tBu,Me} (**10**) type pincer ligands reported by Wanbin Zhang,[10,21] and the PNP^{Cy,Me} (**11**) type pincer ligand reported by Mezzetti.[4n,22] Since alkyl substituted phosphines are sensitive to both air and moisture, these ligands are protected by boranes, and the boranes need to be removed first when coordinate them with metals.

2.1.2 Asymmetric catalytic synthesis. In 2006, Toste *et al.*[23] developed a new procedure to synthesize P-stereogenic pincer ligands: a nucleophilic ruthenium phosphido complex mediates asymmetric catalytic synthesis (Scheme 2). They used the (*R*)-^{i}Pr-PHOX–Ru complex as catalyst, catalyzed the alkylation of methylphenylphosphine **12** by 2,6-bis(chloromethyl)pyridine **13a** and 1,3-bis(chloromethyl)benzene **13b** to obtain the PNP^{tBu,Ph} (**6**) and PCP^{tBu,Ph} (**7**) pincer ligands with 84% (**6**) and 95% ee (**7**) (Scheme 2), respectively.

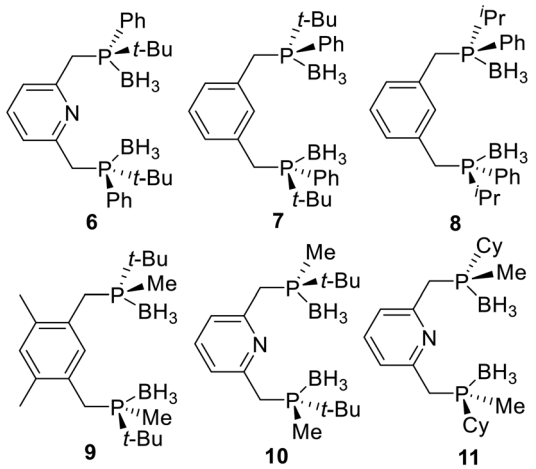


Fig. 3 Classical P-stereogenic pincer ligands synthesized by condensation of P-stereogenic synthons and halohydrocarbons.

This enantioselective alkylation reaction provided an efficient access for useful and synthetically challenging P-stereogenic pincer ligands in a single step from secondary phosphines and alkyl halides. Analogously, Duan *et al.*[8j] developed a PCP type pincer–Pd complex catalyzed asymmetric alkylation of methylphenylphosphine with alkyl halides, which could be efficiently used to synthesize the P-stereogenic pincer ligands.

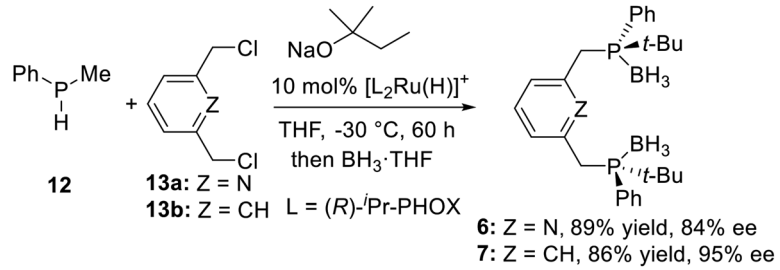
2.1.3 Diastereomeric resolution. Since the method to introduce the chirality in P-stereogenic PCP type pincer ligands could not be easily adopted and applied to the synthesis of optically active P-stereogenic POCOP type pincer ligands, Guan *et al.*[24] developed a new approach: firstly, synthesize a diastereomeric mixture of a POCOP type pincer ligand, followed by cyclometalation with $NiCl_2$ and separation of the resulting nickel pincer complex (Scheme 3, top). The ligand 1,3-[(^{t}Bu)(Ph)PO]$_2$C$_6$H$_4$ (**15**) was prepared in 85% yield from doubly deprotonated resorcinol and commercially available racemic PhP(^{t}Bu)Cl. The ^{31}P NMR spectrum of **15** suggesting a 1 : 1 ratio of the racemic and meso isomers.[24] Cyclometalation of **15** with $NiCl_2$ give a 1 : 1 mixture of the racemic and meso pincer chloride complexes **16**-*rac* and **16**-*meso*.

Repeated recrystallization of **16** from 1 : 1 CH_2Cl_2/pentane provided **16**-*rac* with high isomeric purity (98%). Removal of the solvent from the mother liquor yielded a **16**-*meso*-enriched sample (80–93%). Then they attempted to resolve the enantiomers of **16**-*rac* by removal of the chloride ligand with AgOTf followed by substitution with a chiral carboxylate (Scheme 3, bottom). (*S*)-*O*-acetylmandelate and gibberellate were chosen as the chiral auxiliaries. Unfortunately, despite different solvents and solvent combinations for recrystallization trials, there was no appreciable separation of the diastereomers of **18a** or **18b**.

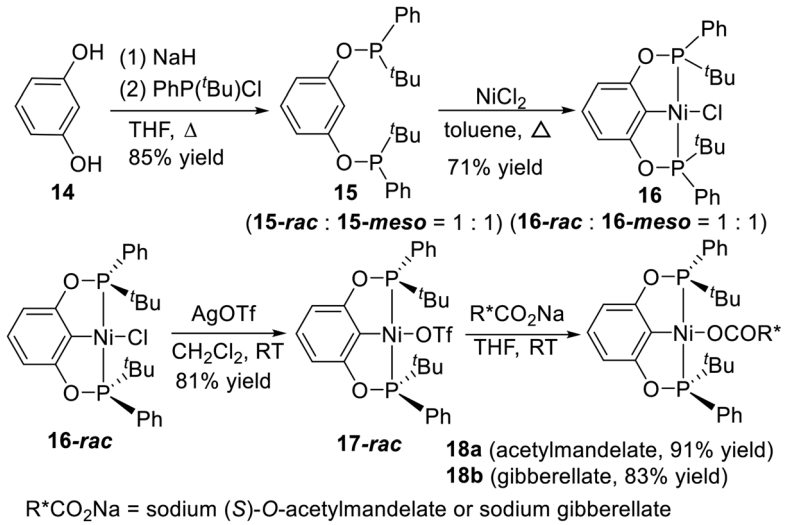
2.2 Synthesis of the non-classic P-stereogenic pincer ligands

All the non-classical P-stereogenic pincer ligands reported so far are POCOP type pincer ligands. The synthesis of this kind of ligand was through phosphorylation of resorcinol derivatives by P-stereogenic synthons, such as the pincer type phosphodiamidite ligand reported by Gavrilov[11] in 2009. They used the (2*R*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0] octane (**19**) as the P-stereogenic synthon, adopting a one-step phosphorylation of resorcinol **14** in the presence of Et_3N and PhMe (Scheme 4), and gave the target ligand **20** in 70% yield.

In 2010, Gebbink *et al.*[25] reported a series of novel P-stereogenic bis-phosphoramidite pincer ligands derived from chiral amino alcohols. The optically active amino alcohol was phosphonated by PCl_3 in the presence of triethylamine to afford the corresponding phosphorochloridate adduct **21**, which was subsequently coupled with 2-iodoresorcinol **22** in toluene at 110 °C to yield P-stereogenic pincer arene ligand **23** in good yield (Scheme 5, top). The diastereomeric ratio (dr) of a sample of crude **23** in solution after filtration was roughly estimated as 98 : 2 by comparing the integral values in the ^{31}P NMR of the two phosphoramidite diastereoisomers. Following a similar synthesis route as reported for **23**, the corresponding phosphorochloridate **24** was subsequently reacted with 2-



Scheme 2 Synthesis of P-stereogenic pincer ligands by asymmetric catalytic synthesis.

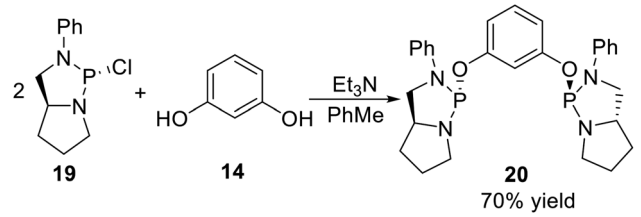


Scheme 3 Synthesis of P-stereogenic pincer ligands by diastereomeric resolution.

iodoresorcinol **22** at 110 °C to yield pincer arene ligand **25** in good yield and acceptable purity after a simple filtration (Scheme 5, bottom). The diastereomeric ratio of crude **25** in solution after filtration was roughly estimated at 95 : 5 by comparing the integral values of the ^{31}P NMR signals.

3. Synthesis of P-stereogenic pincer complexes

Pincer ligands are a kind of tridentate ligands with strong rigidity, which can easily form stable complexes with transition metals. P-stereogenic pincer ligands coordinate with transition metals in four main ways: C–H activation, oxidative addition, transmetalation, and direct coordination.

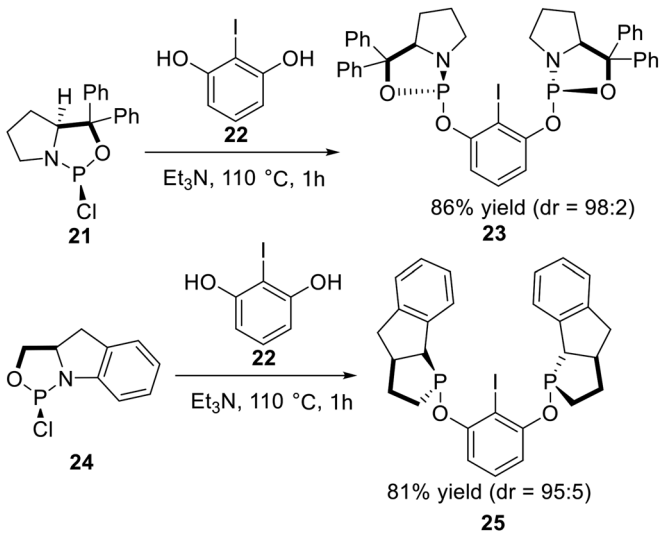


Scheme 4 Synthesis of the non-classic P-stereogenic pincer ligands reported by Gavrilov.

3.1 Synthesis of P-stereogenic pincer complexes *via* C–H activation

Metalation of pincer ligands by appropriate metal precursors *via* C–H activation is an efficient approach to synthesize P-stereogenic pincer–metal complexes. van Koten and coworkers reported the first P-stereogenic pincer–metal complex in 2001 by C–H activation.[19a] The borane protected P-stereogenic pincer ligand **7** was deprotected in alkaline conditions to give ligand **26** (Scheme 6). Stirring the freshly deprotected ligand **26** with $[Pd(MeCN)_4][BF_4]_2$ in MeCN generated the P-stereogenic pincer–Pd complex **27** through C–H activation in 15% yield from **7**. The complex **27** has been characterized by multinuclear (^{1}H, ^{13}C, ^{31}P) NMR and polarimetry. Crystallization of **27** from CH_2Cl_2/hexane produced single crystals suitable for X-ray crystallography. The X-ray crystallography data showed that this P-stereogenic pincer–Pd complex had approximately a C_2 symmetry structure.

This route is the most common method to synthesize P-stereogenic pincer–metal complexes, and many complexes were synthesized by this method. Later in 2002, Morales-Morales *et al.*[20] reported the Ph and ^{t}Bu substituted P-



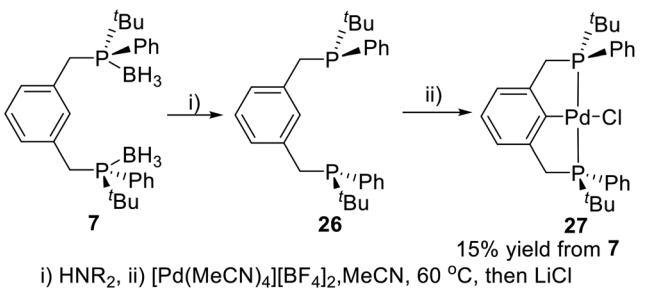
Scheme 5 Synthesis of the non-classic P-stereogenic pincer ligands reported by Gebbink.

stereogenic PCP type pincer ligand **26** and its palladium complex **27**. He also used the ligand **26** to coordinate with $[IrCl(COE)_2]_2$ and obtained a PCP type P-stereogenic pincer–Ir complex **28** *via* C–H activation (Scheme 7). Goldman *et al.*[26] synthesized an unsymmetrical PCP type P-stereogenic pincer–Ir complex **30** based on this approach in 2009. In this complex, one phosphorus is substituted by two ^{t}Bu, the other phosphorus is substituted by one ^{t}Bu and one Me. He only made the racemic complex. Similarly, the racemic POCOP type P-stereogenic pincer–Ni complex **32** reported by Guan *et al.*[24] was synthesized by the same approach.

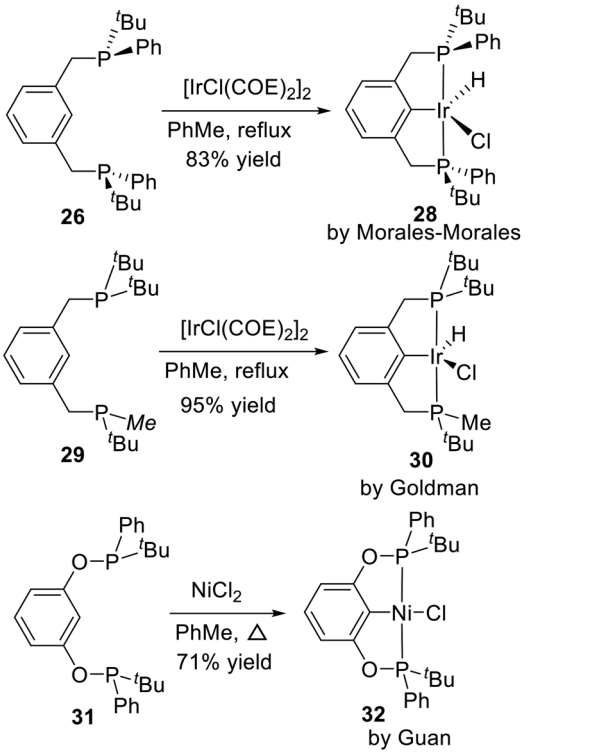
In 2010, Song *et al.*[27] synthesized a series of P-stereogenic pincer complexes from easily available starting materials in a four-component (including diphenylprolinol, PCl_3, resorcinol, and $PdCl_2$), one-pot manner, as shown in Scheme 8. Firstly, the optically active amino alcohol (*S*)-diphenyl(pyrrolidin-2-yl) methanol (**33**) was phosphonated with PCl_3 in the presence of triethylamine in DCE (1,2-dichloroethane) to afford the expected phosphorochloridate adduct (**21**). Then the adduct reacted *in situ* with resorcinol, followed by treatment with $PdCl_2$. The pure air- and moisture-stable complex **34a** was successfully obtained in 35% isolated yield (based on resorcinol) as a white solid after chromatography on silica gel. Using more hindered 4,6-di-*tert*-butylbenzene-1,3-diol instead of resorcinol as a backbone, the complex **34b** was obtained in 20% yield with a similar process.

Displacement of one phospholidine cycle at the 2- or 6-position of the central aryl ring in the symmetrical complexes **34a** and **34b** by a chiral imidazoline unit, Song *et al.*[6i,27] also synthesized an unsymmetrical P-stereogenic pincer–Pd complex and a pincer–Ni complex (Scheme 9). Following a synthetic route similar to that for complexes **34a** and **34b**, the adduct obtained from treatment of (*S*)-diphenyl(pyrrolidin-2-yl)methanol with PCl_3 was reacted *in situ* with the imidazolinyl-containing *m*-phenol derivative **35**. The subsequent palladation also proceeded *in situ* by the addition of $PdCl_2$. The unsymmetrical Pd(II) complex **36a** was successfully isolated as a yellow solid after chromatography on silica gel in 42% yield. Nickelation of the related preligand with $NiCl_2$ instead of $PdCl_2$, the corresponding PCN–pincer Ni(II) complex **36b** could also be obtained *via* C–H activation as a pale yellow solid after chromatography on silica gel, albeit in a lower yield (20%).

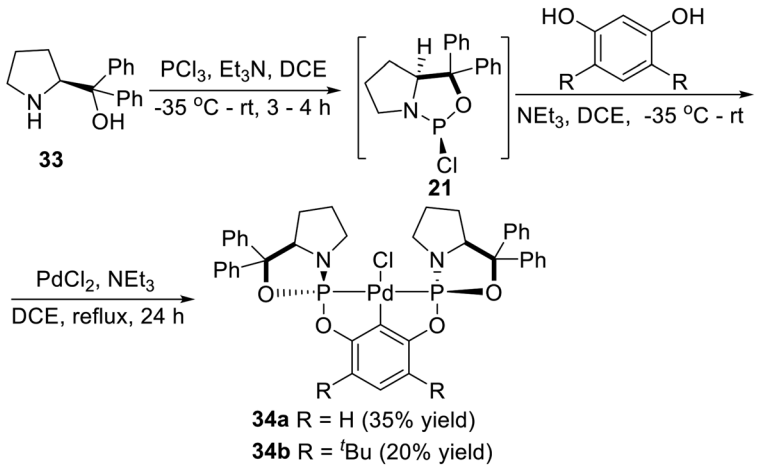
In 2013, Wanbin Zhang *et al.*[21a] developed a novel PCP type P-stereogenic pincer ligand **37** with P(^{t}Bu)Me as the chiral center (Scheme 10). In this ligand, the phosphorus was substituted by one Me and one ^{t}Bu, with a very large steric difference. The P-stereogenic PCP-type pincer–metal complexes were prepared in two steps using an optimal "one-pot" procedure. First, the boranes in compound **37** were removed using trifluoromethanesulfonic acid (TfOH) in degassed toluene,



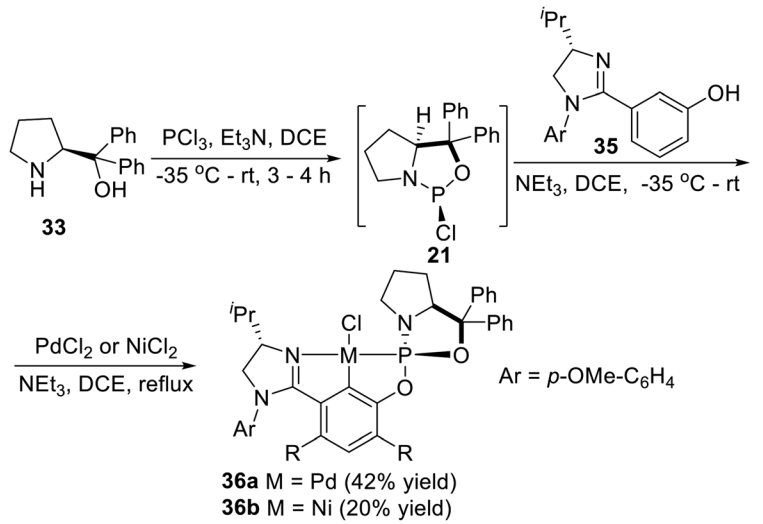
Scheme 6 Synthesis of P-stereogenic pincer–Pd complex *via* C–H activation reported by van Koten.



Scheme 7 Synthesis of P-stereogenic pincer–Ir and pincer–Ni complexes by C–H activation.



Scheme 8 Synthesis of P-stereogenic pincer–Pd complexes *via* C–H activation reported by Song.

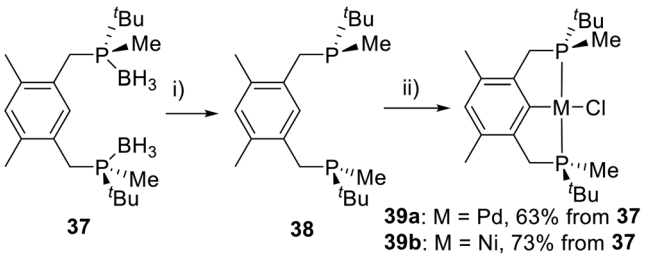


Scheme 9 Synthesis of the unsymmetrical P-stereogenic pincer–metal complexes *via* oxidative addition reported by Song.

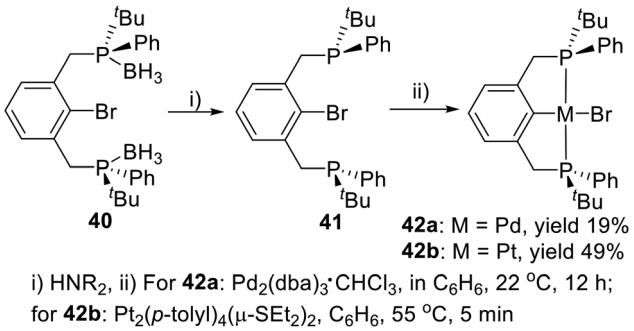
followed by reaction with aqueous KOH in degassed ethanol to produce bisphosphine **38**. Ligand **38** was then directly reacted with bis(acetonitrile)dichloropalladium(II) or nickel(II) chloride hexahydrate[10] *via* C–H bond activation in toluene or a mixed solvent system of ethanol and water to give the P-stereogenic PCP type pincer–Pd complex **39a** or pincer–Ni complex **39b**. The total yields from **37** to **39a** and **39b** were 63% and 73%, respectively. The resulting solid is stable to air and moisture and does not require any special storage procedures.

3.2 Synthesis of P-stereogenic pincer complexes *via* oxidative addition

Except for the tertiary butyl and phenyl substituted PCP type P-stereogenic pincer ligand **7**, van Koten and coworkers[19a] also synthesized a similar ligand (**40**) with a bromine substituted on the iso-carbon (Scheme 11). The phosphine–boranes in **40** can be deprotected with an excess of various types of amines to give ligand **41**. The freshly deprotected **41** dissolved in benzene and reacted with $Pd_2(dba)_3{\cdot}CHCl_3$ over the course of 12 h to generate the pincer–Pd complex **42a** *via* oxidative addition in 19% yield. The product was filtered through silica in ether. Correspondingly, react the deprotected ligand **41** with Pt_2(*p*-



Scheme 10 P-stereogenic pincer complexes reported by Wanbin Zhang.



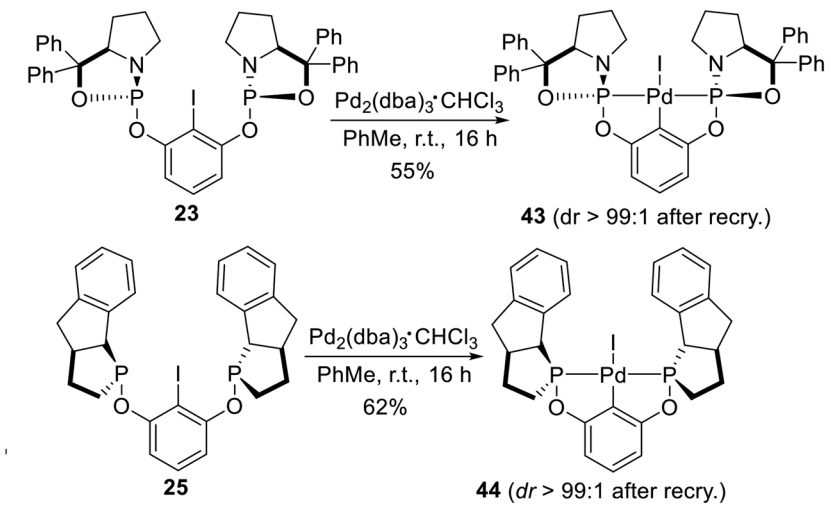
Scheme 11 Synthesis of P-stereogenic pincer complexes *via* oxidative addition reported by van Koten.

tolyl)$_4$(μ-SEt$_2$)$_2$ in benzene generated the pincer–Pt complex **42b** in 49% yield.

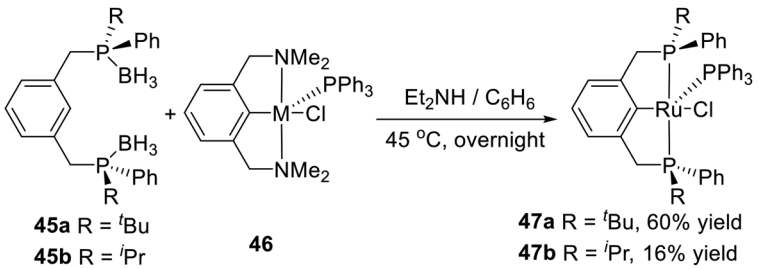
The chiral amino alcohol derived bis-phosphoramidite non-classical pincer–Pd complexes reported by Gebbink *et al.*[25] were synthesized by oxidative addition too. The ligand **23** and **25** have an iodine substituted on the iso-carbon (Scheme 12). Palladation of pincer ligand **23**, with complete retention of the stereospecificity, was achieved *via* an oxidative addition reaction of **23** with a zerovalent Pd species (*i.e.*, Pd$_2$(dba)$_3$·CHCl$_3$) under mild conditions (rt, 16 h). The pincer–palladium complex **43** was obtained in reasonable yield (55%) and with excellent diastereoselectivity (dr > 99 : 1) after fractional crystallization from concentrated CH_2Cl_2 solution by the addition of hexanes. Following a similar synthesis route as that reported for **43**, palladation of the resulting pincer aryl iodide ligand **25** was smoothly achieved through oxidative addition with Pd$_2$(dba)$_3$·CHCl$_3$ under mild conditions (rt, 16 h). Complex **44** was obtained in promising yield (62%) with excellent diastereoselectivity (dr > 99 : 1) after fractional recrystallization from CH_2Cl_2/hexanes.

3.3 Synthesis of P-stereogenic pincer complexes *via* transcyclometalation

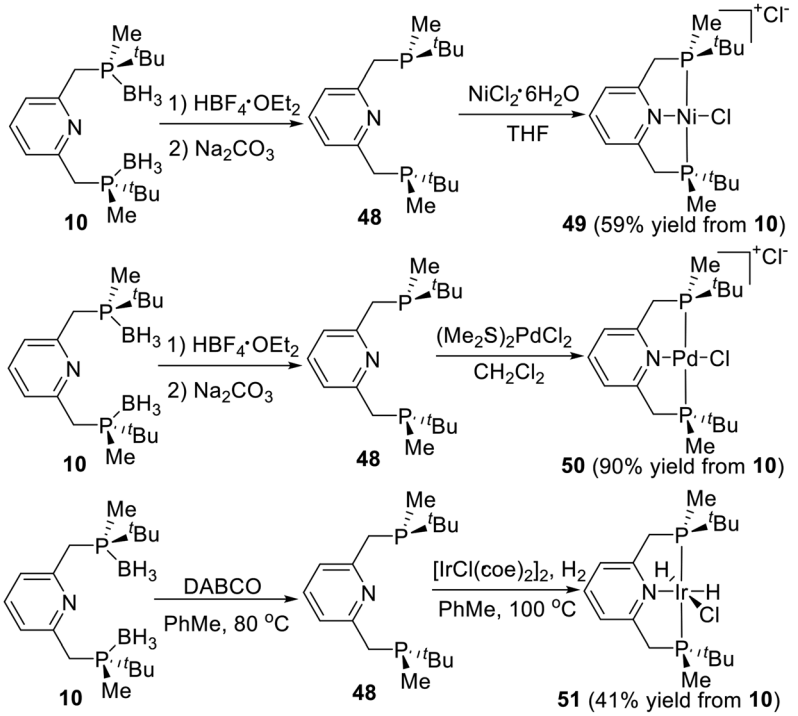
In 2005, van Koten *et al.* synthesized two kinds of PCP type P-stereogenic pincer–Ru complexes in a direct one-pot synthesis,[19b] the deprotection of the prepared phosphine–boranes **45a** or **45b** and the subsequent transcyclometalation (Scheme 13). Deprotection of the phosphine–boranes was easily accomplished by overnight heating of a benzene solution of **45a** or **45b** in the presence of an excess of Et_2NH at 45 °C. Complex **46** was then added and stirred for 24 h. Complex **47a** was isolated as a relatively air-stable, ink-blue solid in 60% yield. Complex **47b** was obtained pure in low yield (16%) after several purification steps as an air-sensitive, deep green, crystalline solid. This



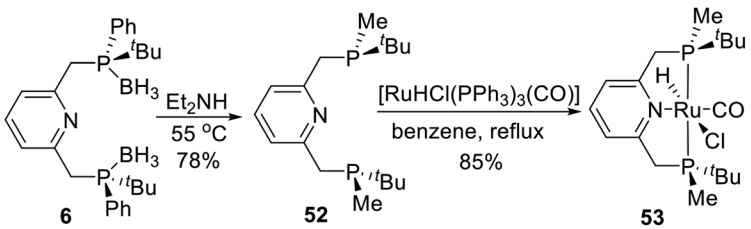
Scheme 12 Synthesis of P-stereogenic pincer complex *via* oxidative addition reported by Gebbink.



Scheme 13 Synthesis of P-stereogenic pincer complexes *via* transcyclometalation.



Scheme 14 Synthesis of P-stereogenic pincer complex *via* direct coordination reported by Wanbin Zhang.

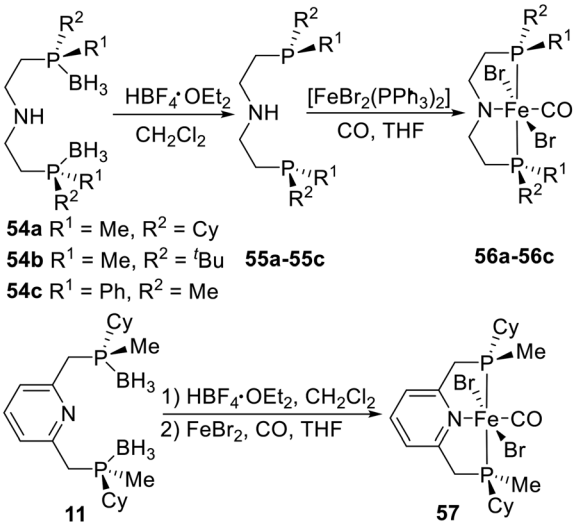


Scheme 15 Synthesis of P-stereogenic pincer complex *via* direct coordination reported by Castillón.

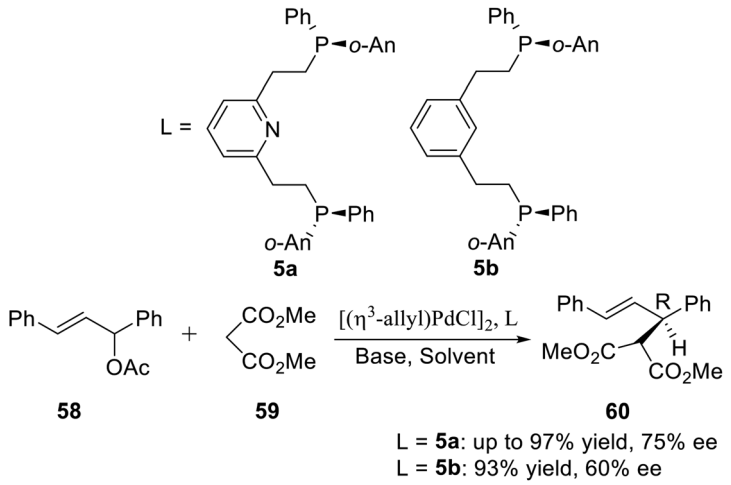
report provided a new approach to synthesize pincer–metal complexes.

3.4 Synthesis of P-stereogenic pincer complexes *via* direct coordination

PNP type pincer ligand is a deeply researched tridentate ligand, which is easy to coordinate with transition metals directly. Wanbin Zhang *et al.*[21d] adopted the Livinghouse's deprotection method[28] to prepare a series of P-stereogenic PNP type pincer–metal complexes over two high-yielding steps (Scheme 14). Thus, the borane groups were removed *via* the reaction of (*R*,*R*)-2,6-bis-[(boranato(*tert*-butyl)methylphosphino)methyl]pyridine (**10**) with tetrafluoroboric acid diethyl ether in degassed dry dichloromethane, followed by treatment with degassed 10% Na_2CO_3 solution to produce the resulting bisphosphine pyridine **48.** Ligand **48** directly reacted with nickel(II) chloride hexahydrate in THF at ambient temperature to afford the cationic complex **49** as a red solid,[10] which was obtained in 59% yield from **10.** The ligand **50** then reacted directly with



Scheme 16 Synthesis of P-stereogenic pincer complex *via* direct coordination reported by Mezzetti.



Scheme 17 $PNP^{o\text{-}An,Ph}$ pincer–Pd complexes catalyzed asymmetric allylic alkylation.

$(Me_2S)_2PdCl_2$ in degassed dry dichloromethane to form the P-stereogenic pincer–Pd complex **50** as an orange solid in 90% total yield.[21d] The ligand **50** reacted with $[IrCl(coe)_2]_2$ under hydrogen pressure to give the pincer–iridium complex **51** as a white solid in 41% yield.[21c] All of the resulting solid products are stable to air and moisture and required no special storage precautions.

In 2015, Castillón *et al.*[29] reported a novel P-stereogenic $PNP^{tBu,Ph}$ ruthenium complex *via* direct coordination the pincer ligand and ruthenium precursor. The straightforward synthesis of **53** was accomplished in two steps, starting from phosphine–borane complex **6** (Scheme 15). After trying many deprotection methods, ligand **52** was finally obtained in good yield (78%) by reaction with an excess of diethylamine and purification by preparative TLC inside a glove-box. The use of alumina instead of silica plates and careful anhydrous handling were crucial in order to obtain reproducible experiments. The resulting ligand was treated with $[RuHCl(PPh_3)_3(CO)]$ in refluxing benzene to afford Ru complex **53** in 85% yield as a pale-yellow solid.

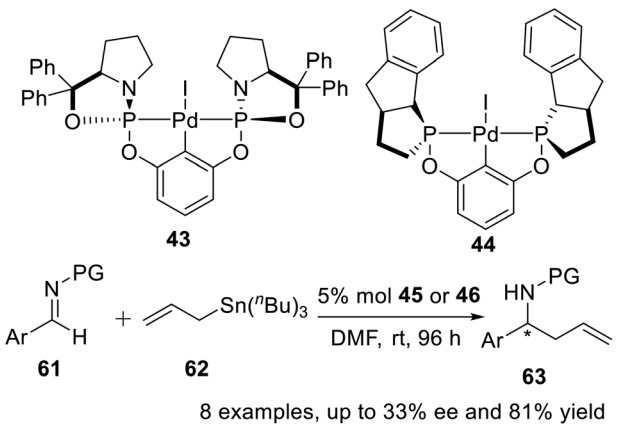
Recently, Mezzetti *et al.*[4n,22] synthesized a series of PN(H)P and PNP type pincer–Fe complexes by a similar coordination strategy. The borane-protected pincer ligands **54a–54c** were indefinitely stable upon storage in air at room temperature and were deboronated with $HBF_4 \cdot OEt_2$ in dichloromethane before complexation (Scheme 16). After workup, the resulting pincer ligands **55a–55c** were reacted with $[FeBr_2(PPh_3)_2]$ in THF to give the target P-stereogenic pincer–Fe complexes.[22] In addition the PN(H)P pincer ligand, they also synthesized the pyridine based PNP pincer ligand **11**. Phosphine–borane **11** was deprotected with $HBF_4 \cdot OEt_2$ in dichloromethane. Treatment of the free ligand with $FeBr_2$ under a CO atmosphere (1.1 atm) gave the deep blue dibromocarbonyl complex **57**, which was precipitated with pentane, filtered in air, and purified by washing with water, ethanol, diethyl ether, and pentane.[4n] Complex **57** is perfectly stable toward air and moisture both in solution and in the solid state. No decomposition was observed after storing solid samples in air at room temperature for several months.

4. P-stereogenic pincer–metal complexes catalyzed asymmetric reaction

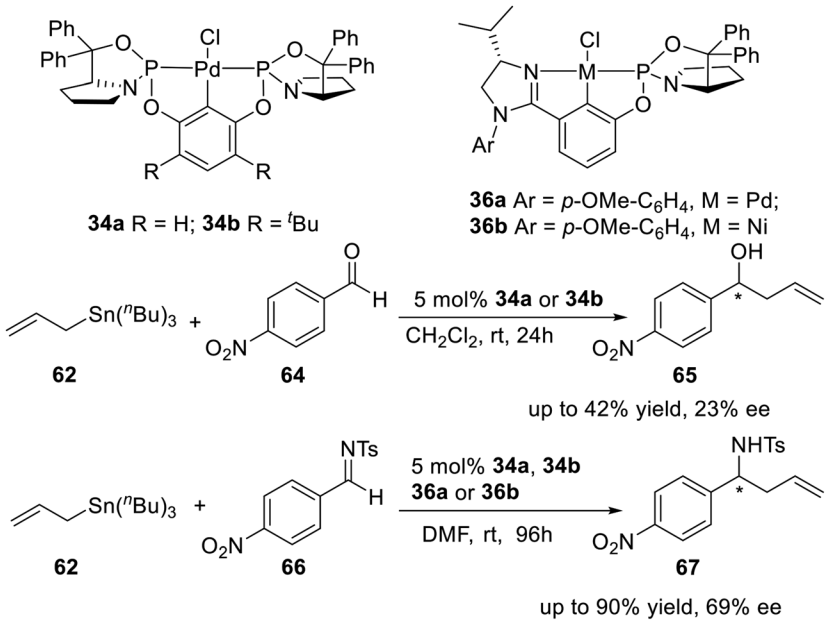
The most important application of P-stereogenic pincer–metal complexes is as chiral metal catalysts to catalyze various asymmetric synthetic reactions. At present, there have been many reports on this field.

4.1 Asymmetric allylic alkylation

Allylic alkylation catalyzed by Pd complexes is an extremely versatile carbon–carbon bond forming reaction. In order to achieve substrate generality, the search for efficient ligand systems continues to receive considerable attention. X. Zhang *et al.*[16a] used the P-stereogenic pincer–Pd complex generated by ligand **5a** or **5b** with $[(\eta^3\text{-allyl})PdCl]_2$ *in situ* to catalyze the asymmetric allylic alkylation between 1,3-diphenyl-2-propenyl acetate and dimethyl malonate (Scheme 17). After examining various bases and solvents, their results indicated that the



Scheme 18 POCOP pincer–Pd complexes catalyzed asymmetric homoallylation of sulfonimines.

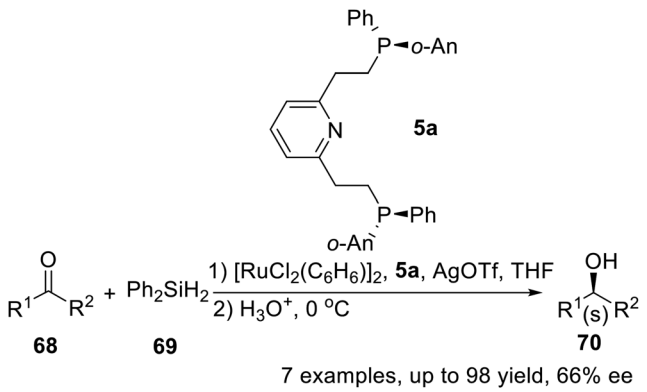


Scheme 19 P-stereogenic pincer–Pd and pincer–Ni complexes catalyzed asymmetric allylation of aldehydes and sulfonimines.

combination of BSA and KOAc in benzene gave the best enantioselectivity (75% ee). This was the first report about the P-stereogenic pincer-complex catalyzed asymmetric reaction. The results showed that the P-stereogenic pincer-catalyst is a very promising chiral catalyst.

Gebbink *et al.*[25] reported two novel P-stereogenic pincer–metal complexes in 2010, and embarked on testing the stereocontrolling potential of the two novel complexes **43** and **44**. These tests were carried out for the reaction of allyltributyltin with sulfonimines, *i.e.*, with protected aryl aldimines, at room temperature in dry DMF without additives (Scheme 18). The bisphosphoramidite pincer–palladium complexes **43** and **44** were active catalysts for asymmetric homoallylation of sulfonimines, where low (up to ee 33%) or no enantioselectivity was observed for reactions catalyzed by **43** and **44**, respectively. Preliminary catalytic results revealed that enantiomeric excess values varied by using differently functionalized sulfonimines, suggesting that both electronic properties and steric congestion of sulfonimines affected the transition state of the electrophilic attack of the $^1\eta$-allyl Pd intermediate in the allylation.

The same year, Song and coworkers[6i,27] synthesized four P-stereogenic pincer–Pd and pincer–Ni complexes **34a**, **34b**, **36a**, and **36b** (Scheme 19), in which the P-stereogenic pincer ligands were coordinated to palladium (**34a, 34b** and **36a**) or nickel (**36b**). They used these complexes to catalyze the asymmetric allylation of 4-nitrobenzaldehyde or 4-nitrobenzenesulfonimine. They obtained up to 42% yield and 23% ee to 4-nitrobenzaldehyde and up to 90% yield and 69% ee to 4-nitrobenzenesulfonimine, respectively.



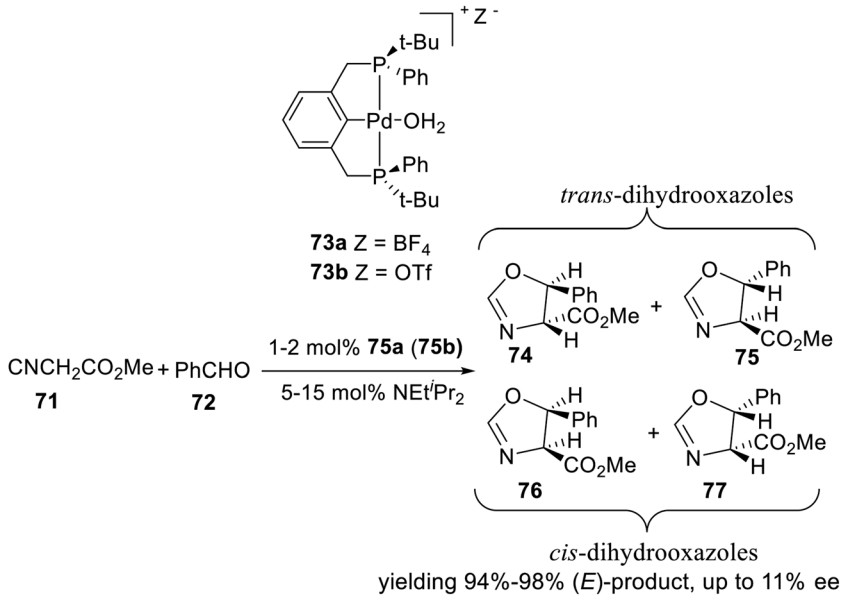
Scheme 20 PNP$^{o\text{-An,Ph}}$ pincer–Ru complexes catalyzed asymmetric hydrosilylation.

4.2 Asymmetric hydrosilylation

In 1997, X. Zhang and his team conducted a follow-up study on P-stereogenic pincer ligand **5a**, which was employed as chiral ligand combined with Ru to catalyze the asymmetric hydrosilylation of several aryl alkyl ketones.[16b] They had performed asymmetric hydrosilylations of ketones under optimum conditions (Scheme 20). Typically, 1 mol% of ruthenium catalyst was used with 2.2 mol% of the chiral tridentate ligand. Enantioselectivities ranging from **47** to 66% were observed and the reactions occurred with excellent conversions (isolated yields from 85 to 98%). These values are the best results reported to date with ruthenium catalysts.

4.3 Asymmetric aldol condensation

The asymmetric aldol condensation of methyl 2-isocyanoacetate and benzaldehyde is an effective reaction to synthesize chiral dihydrooxazoles. This reaction is interesting both because it is a potential route to β-hydroxy-amino acids, and because it involves the formation of a C–C bond with simultaneous creation of two chiral centers, resulting in four possible



Scheme 21 Aldol condensation of methyl 2-isocyanoacetate and benzaldehyde.

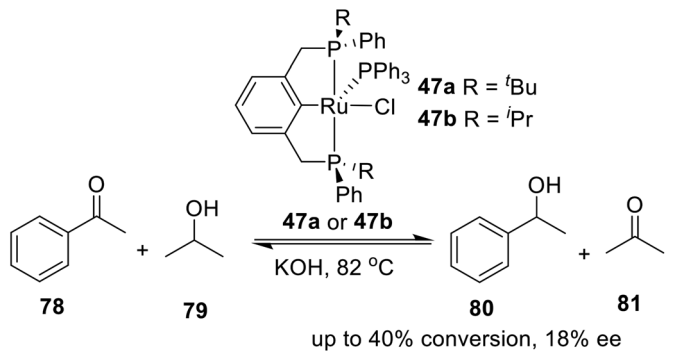
stereoisomers. It is thus a useful test reaction for exploring the chiral induction provided by new, chiral Lewis acid catalysts. In 2001, van Koten and coworkers synthesized two P-stereogenic pincer–Pd complexes **73a** and **73b** (Scheme 21), and did an initial test reaction between methyl 2-isocyanoacetate and benzaldehyde. Indeed, for the Pd complexes **73**, the diastereoisomeric ratio was found to be higher, yielding 94–98% (*E*)-product. However, the enantiomeric excess was never found to be higher than 11%. Variations of the concentration of catalyst, aldehyde, and base did not appreciably affect the enantioselectivity, nor did changing the reaction solvent from CH_2Cl_2 to THF or toluene.

4.4 Asymmetric hydrogen transfer reaction

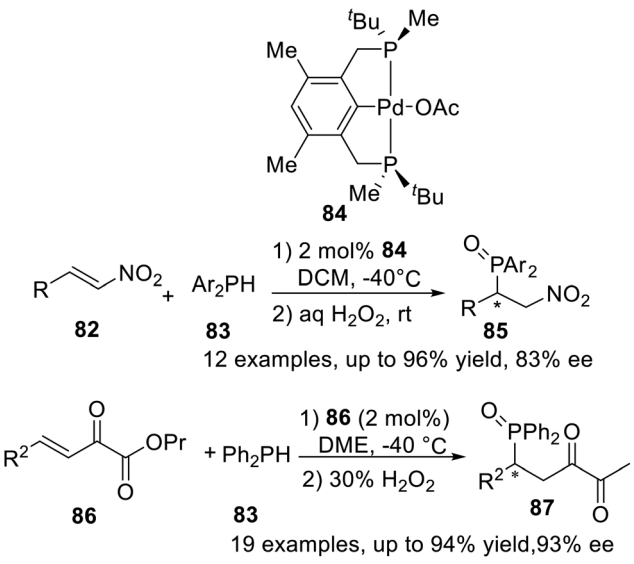
In 2005, van Koten and coworkers[19b] designed and synthesized a kind of P-stereogenic $PNP^{tBu,Ph}$ ruthenium pincer complex and applied it in asymmetric reduction of ketones with propan-2-ol. As a result, a moderate yield (up to 40%) and low enantioselectivity (up to 18%) were obtained (Scheme 22). Apparently, the chiral pocket of the catalyst precursors allows for transfer of dihydrogen to both faces of the substrate equally well. Moreover, epimerization at the stereogenic P-centers under the conditions applied during the catalytic experiments cannot be excluded. The preliminary catalysis results showed that although the novel chiral ruthenium complexes were moderately active, the chiral induction was lost upon prolonged reaction.

4.5 Asymmetric Michael addition

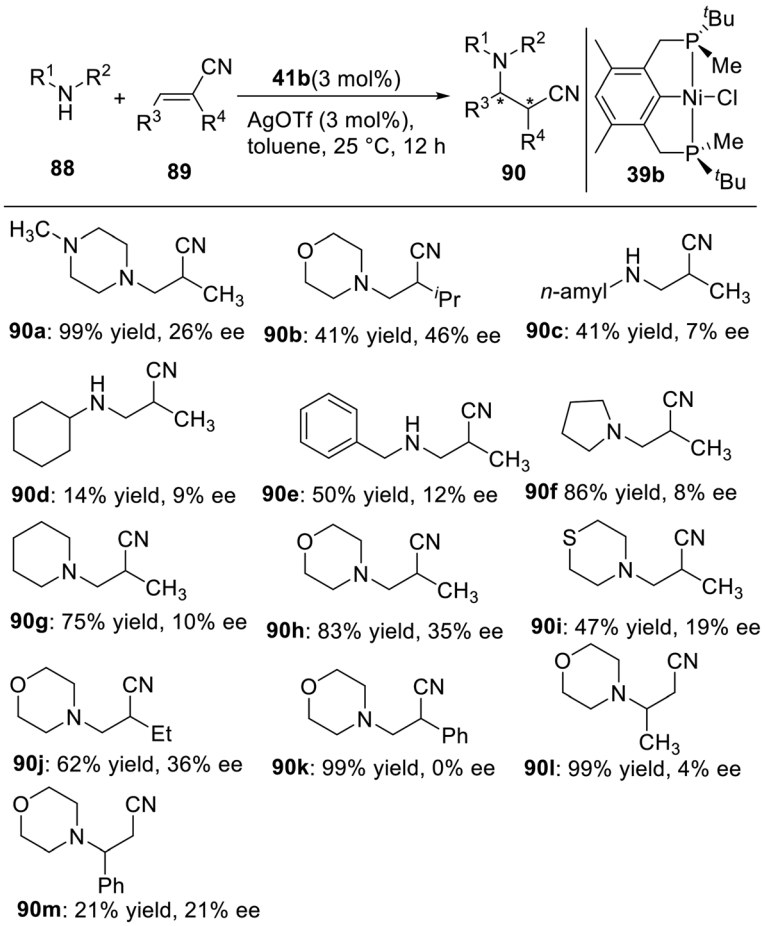
The catalytic asymmetric construction of P–C bonds is considered to be one of the most powerful methods for the preparation



Scheme 22 Hydrogen transfer reaction of acetophenone by ruthenium.



Scheme 23 Pincer–Pd catalyzed asymmetric Michael addition of diarylphosphine to nitroalkenes and β,γ-unsaturated α-ketoesters.



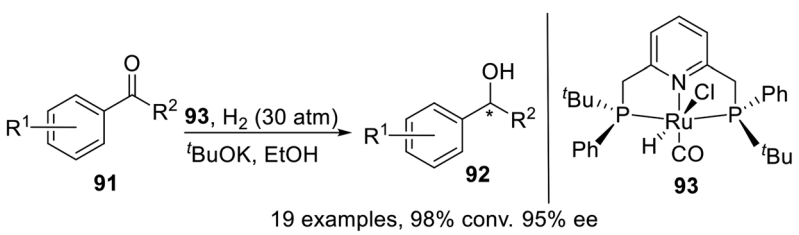
Scheme 24 P-stereogenic pincer–Ni catalyzed asymmetric aza-Michael reaction.

of chiral organophosphorus compounds. In 2013, Wanbin Zhang *et al.*[21a] used the P-stereogenic PCP type pincer–Pd complex **84** to catalyze the asymmetric Michael addition of diarylphosphines to nitroalkenes, obtained up to 96% yield and 83% ee within 12 examples (Scheme 23). And then in 2015,[21b] the asymmetric Michael addition of diphenylphosphine to β,γ-unsaturated α-keto esters was successfully processed by the same catalyst, obtained in up to 94% yield and 93% ee.

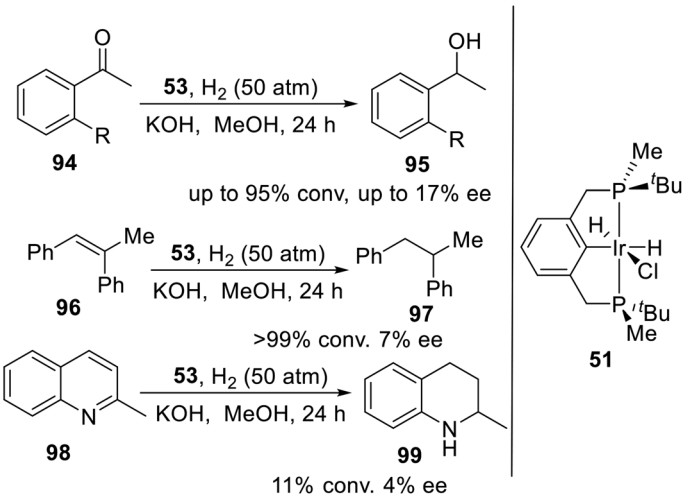
In 2015, Wanbin Zhang *et al.* developed a series of new P-stereogenic pincer–nickel complexes in 55–84% yields by using a flexible synthetic approach.[10] These complexes were fully characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ^{19}F NMR, and/or single-crystal X-ray diffraction. These complexes were shown to be active catalysts for the aza-Michael addition of α,β-unsaturated nitriles (Scheme 24), providing the products in good to excellent yields (up to 99%) and with moderate enantiomeric excesses (up to 46% ee). Notably, the PCP complex exhibited higher catalytic activity in the aza-Michael addition than the PNP complexes.

4.6 Asymmetric hydrogenation

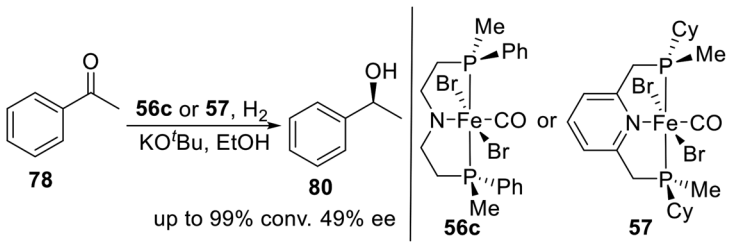
In 2015, Castillón *et al.*[18] synthesized and characterized the first P-stereogenic PNP$^{t\mathrm{Bu,Ph}}$–Ru complex which had been proven to be an efficient catalyst for the asymmetric reduction of a variety of aromatic and heterocyclic ketones (Scheme 25). Although the enantioselectivities obtained were not superior to those



Scheme 25 PNP$^{t\mathrm{Bu,Ph}}$ Pincer–Ru complexes catalyzed asymmetric hydrogenation.



Scheme 26 PNP^{tBu,Me} pincer–Ir complexes catalyzed asymmetric hydrogenation.



Scheme 27 P-stereogenic pincer–Fe catalyzed asymmetric hydrogenation of acetophenone.

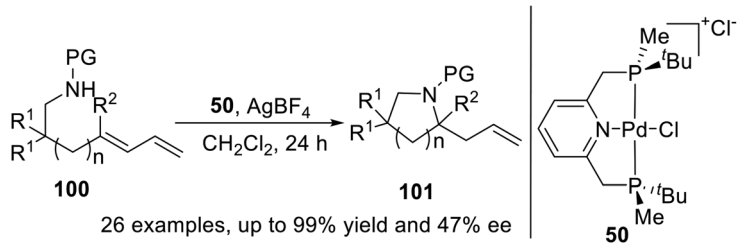
reported for other commercially available catalysts, this catalyst, active under very mild operating conditions, could be of significant interest in the chemoselective reduction of ketones in the presence of typical functional groups.

Wanbin Zhang and coworkers[21c] had designed and synthesized a novel P-stereogenic pincer–iridium complex **53** in reasonable yields using a short synthetic route. This complex was used as catalyst in the hydrogenation of ketones, olefins and quinoline derivatives to provide the desired products with moderate to excellent conversions (up to 99%) and up to 17% enantiomeric excess (Scheme 26).

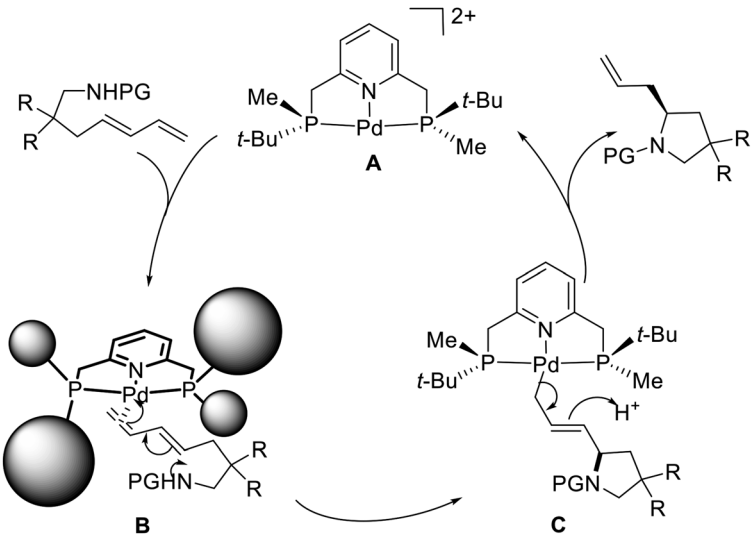
In 2018, Mezzetti *et al.* developed a series of P-stereogenic PN(H)P pincer ligands and their iron(II) derivatives by DFT-driven ligand design.[22] These complexes were efficient catalysts in asymmetric hydrogenation of acetophenone (Scheme 27). In the same year, they reported a tridentate, P-stereogenic, C_2-symmetric PNP pincer ligand and its iron(II) complex **57**.[4n] In the presence of base, bromocarbonylhydride **57** catalyzes the hydrogenation of acetophenone to (*S*)-1-phenylethanol with 49% ee. The density functional theory (DFT) calculations show that the outer-sphere monohydride mechanism reproduces the experimentally observed sense of induction (*S*) and enantioselectivity, whereas the dihydride and inner-sphere pathways predict the formation of the *R* enantiomer.

4.7 Intramolecular hydroamination

In 2015, Wanbin Zhang and coworkers[21d] prepared a novel P-stereogenic PNP pincer–Pd complex from optically pure 2,6-bis [(boranato(*tert*-butyl)-methylphosphino)methyl]pyridine and used



Scheme 28 P-stereogenic pincer–Pd catalyzed asymmetric intramolecular hydroamination.



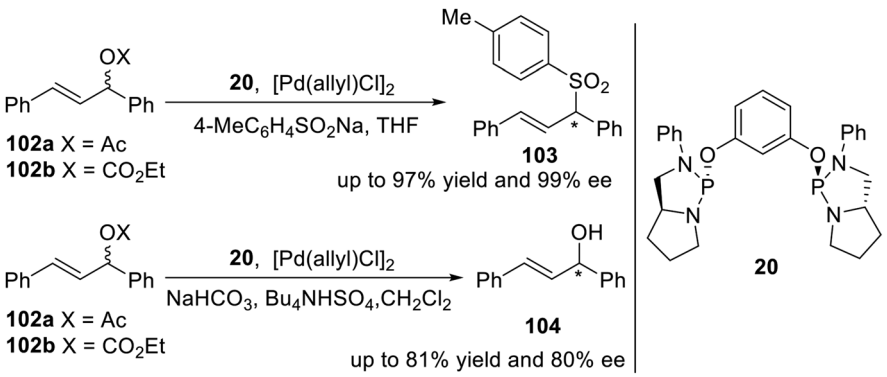
Scheme 29 Proposed reaction pathway of P-stereogenic pincer–Pd catalyzed asymmetric intramolecular hydroamination.

it in the asymmetric intramolecular hydroamination of amino-1,3-dienes (Scheme 28). The desired products were obtained in high yields (up to quantitative yield) and with excellent regioselectivities (>99 : 1) and up to moderate enantioselectivities (up to 47% ee). The absolute configuration of an enantioenriched product was determined by X-ray crystallography studies.

A proposed mechanism has been suggested to explain the excellent regioselectivity of the intramolecular hydroamination (Scheme 29).[21d] Initially, the chiral pincer-type catalyst **50** reacts with $AgBF_4$ to give an activated catalytic molecule **A**. This cationic palladium species interacts with the terminal double bond of the amino-1,3-diene in close proximity the methyl group located on the phosphorus atom due to the strong steric hindrance of the *tert*-butyl group, affording the square planar π-complex **B**. The intermediate **B** undergoes an intramolecular C–N bond formation to produce the η^1-allyl-palladium complex **C**, which is consistent with Michael's discovery of the isolated η^1-allyl-palladium intermediate.[30] Subsequent protonation and cleavage of the Pd–C bond produce the allylic-type *S*-configuration product and regenerate the catalyst **A**. In the absence of a bulky substituent, such as a *tert*-butyl group, the internal double bond of the amino-1,3-diene can also coordinate to the Pd atom of **A**, eventually leading to the undesired propenyl-type product.[31] Because of the remote distance (four bonds) between the palladium atom and the reaction site in **B**, the moderate 43% ee obtained for the allylic-type pyrrolidine derivative presents a very promising result.

4.8 Asymmetric allylic sulfonylation and deracemization

Gavrilov *et al.* reported a pincer type phosphodiamidite ligand **20** containing chiral phosphorus atoms[11] in 2009. To estimate the stereodifferentiating ability of ligand **20** a test reaction of Pd-catalyzed enantioselective allylic sulfonylation of **102a** and **102b** was used (Scheme 30, top). As a result, nearly quantitative chemical yield and stereo-chemical outcome (up to 97% yield and 99% ee) were obtained. Ligand **20** was also involved in an important Pd-catalyzed deracemization reaction of compound **102b** (Scheme 30, bottom) opening access to valuable optically active allylic alcohols, including chalcol **104**. The catalytic system $[Pd(allyl)Cl]_2$/2L (L = **20**) provided good conversion of **102b** (81%) and enantiomeric excess of (*R*)-**104** (80%).



Scheme 30 P-stereogenic pincer–Pd catalyzed asymmetric allylic sulfonylation and deracemization.

5. Conclusion and outlook

Since the pioneering work reported by X. Zhang *et al.* about P-stereogenic pincer ligands in 1996, the chemistry of pincer compounds has achieved great progress. Many strategies have been developed to synthesize P-stereogenic pincer ligands, including classical and non-classical P-stereogenic pincer ligands. The P-stereogenic pincer complexes could be synthesized by C–H activation, oxidative addition, transcyclometalation, and direct coordination in good yields. These kinds of complexes were efficient catalysts in asymmetric catalysis. Many asymmetric reactions could be catalyzed by them, such as allylic alkylation, hydrosilylation, aldol condensation, hydrogen transfer reaction, Michael addition, hydrogenation, hydroamination, allylic sulfonylation and deracemization. In most of the reactions, excellent yields but moderate enantioselectivities were obtained. Further studies should focus on the design and synthesis of P-stereogenic pincer complexes with high asymmetric induction effects.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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