Coordination chemistry and catalysis with secondary phosphine oxides

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Dedicated to Prof. Guillermo Muller on the occasion of his retirement

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XXX PICTURE AUTHORS + CVs

Abstract

Secondary phosphine oxides present a tautomeric equilibrium between the pentavalent oxide form (SPO) and the trivalent phosphinous acid (PA). This dichotomy is the origin of the rich coordination chemistry of this class of compounds. As the pentavalent oxide form usually predominates, SPOs are air-stable but at the same time metal coordination can shift the tautomerism towards the PA form, making the ligand act as an ordinary trivalent phosphine. For this reason this class of ligands have found application in numerous homogeneously catalysed reactions, including some enantioselective transformations. This review aims to give an up to date account on the synthesis, coordination chemistry and homogeneous catalysis with SPOs.

1. Introduction

Tertiary phosphines have been used in the preparation of countless coordination and organometallic complexes since they efficiently bind to a large number of metallic centres providing homogeneous catalysts.[1]

The design of phosphine ligands becomes crucial for the catalytic applications of their metallic precursors. Often, however, these phosphines or even their complexes are difficult to handle, due to their air- and moisture-sensitivity. The preparation of the ligands requires laborious multistep methods often including the use of BH_3 adducts[2] or phosphonium salts.[3] The classical approach employed before of borane adducts was the use of the highly stable phosphine oxides that had to be eventually reduced,

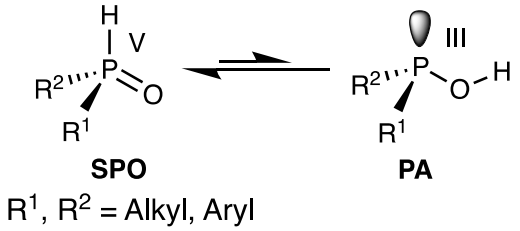
normally using silanes under harsh conditions, incompatible with many functional groups and often leading to racemisation of *P*-stereogenic compounds.

In contrast, a particular type of oxides are Secondary Phosphine Oxides (**SPOs**), which due to their tautomerism with P(III) phosphinous acids (**PAs**) can act as *P*-donor ligands in the presence of transition metal cations. This fact has been known for more than 50 years[4] and the first catalytic applications of SPOs appeared as early in 1986, by van Leeuwen and co-workers.[5] However, this type of ligands received a boost in the early 2000s in cross-coupling chemistry[6] and they currently represent an important, yet underused class of ligand in homogeneous catalysis.

This topic has been previously reviewed but it was either some time ago by Ackermann[7,8] or in a partial way by other authors.[6,9-13] In the present review, the aim is to give an overview of the coordination behaviour of SPOs with transition metals from group 8 onwards which are those that have found more application in catalysis, discussed in the last part. Although the review is not comprehensive, we have attempted to cover the most relevant results in synthesis, coordination chemistry and catalysis with SPOs.

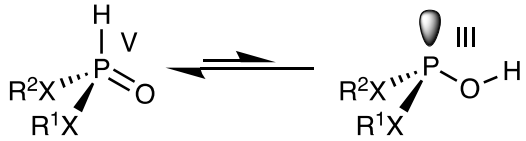
2. Stereoelectronic properties of SPOs

Like the textbook example of keto-enol tautomerism, similar equilibria can be also drawn for some organophosphorus compounds. Secondary Phosphine Oxides (SPOs) and Heteroatom-Substituted Secondary Phosphine Oxides (HASPOs), are of particular interest because they formally contain a pentavalent phosphorus atom ($\sigma^4\lambda^5$), but they can act as potential *P*-donor ligands due to a tautomeric equilibrium with the trivalent phosphinous acid or related compounds ($\sigma^3\lambda^3$) (Scheme 1).



SPO **PA**

R^1, R^2 = Alkyl, Aryl



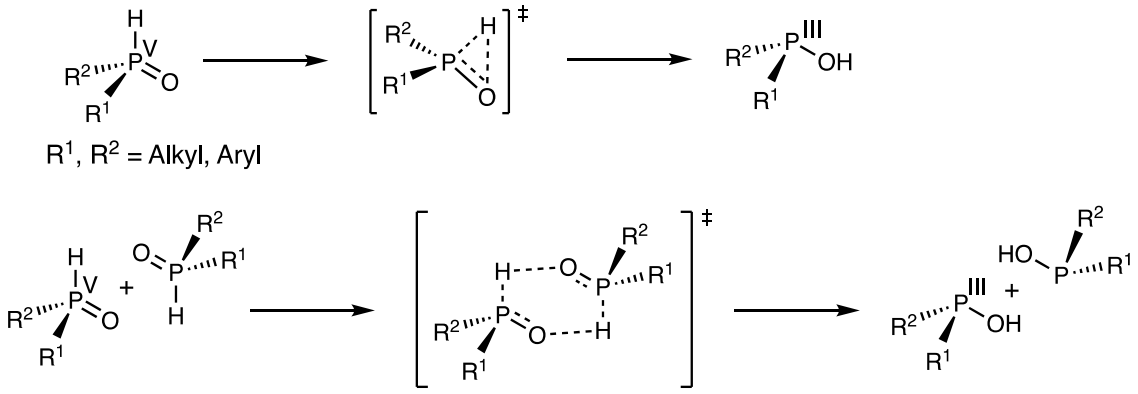
HASPO

R^1, R^2 = Alkyl, Aryl

X = O, NR

Scheme 1. Tautomerism of (HA)SPOs.

The trivalent tautomeric form, a phosphinous acid (PA), is able to bind Lewis acids such as metal ions, and as a result, SPOs are occasionally referred as *preligands*. In general, SPOs are stable towards oxygen, which can be explained by the prevalence of the pentavalent tautomer except in the presence of transition metal cations or silylating agents,[14] which can shift the equilibrium towards the trivalent form. This was proved by deuterium exchange experiments and IR spectroscopic measurements in the 1960s.[15] In 2004, Pietrusiewicz, Duddeck and co-workers suggested[16] from NMR studies that the fast kinetics of the tautomeric equilibrium is due to the migration of an acidic proton. In this line, Hong and co-workers[17] proposed two reaction pathways for the transformation of SPOs to the corresponding PA (Scheme 2), based on DFT calculations.



Scheme 2. Proposed routes for the conversion of SPOs to PAs. Unimolecular pathway (*top*) and bimolecular pathway (*bottom*).

In the unimolecular pathway, the tautomerism takes place due to the intramolecular migration of the hydroxyl proton, whereas in the bimolecular one the conversion can be rationalised by an intermolecular transfer of two hydrogen atoms in a synchronous exchange.

More recently Montchamp and Janesko[18] have shown that the reaction mechanism involves a simultaneous dissociation of a P–H bond and the formation of an O–H bond. The proton exchange which leads to the formal reduction of the P(V) species, can not take place in an intramolecular proton transfer. According to their DFT studies, the unimolecular pathway does not work for those SPOs containing very bulky substituents, since the distorted geometry of the tetrahedral species have very high-energy barriers.

The electronic character of the substituents at the P atom affects the tautomeric equilibrium. In 2010 Börner and co-workers[19] studied the tautomerism of five SPOs with different electronic properties (Figure 1).

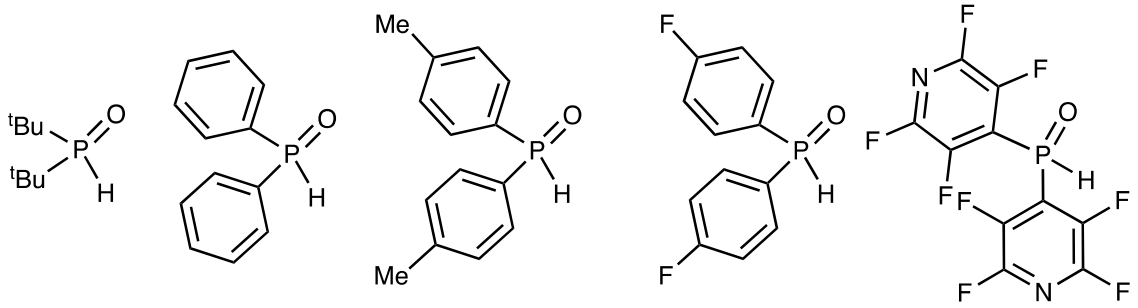
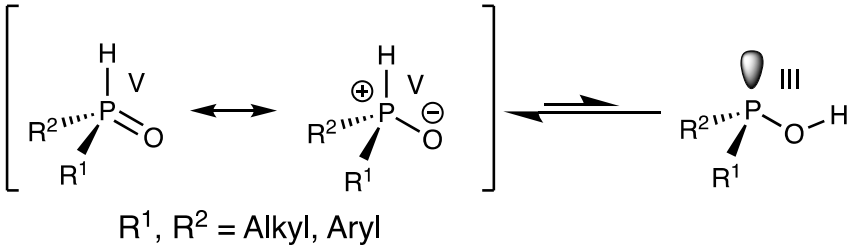


Figure 1. SPOs studied by Börner and co-workers.[19]

They concluded, according to NMR, IR, DFT calculations and X-ray structural analysis that only with strongly electron-withdrawing groups the phosphinous acid form can be observed in the equilibrium, whereas for all the other cases the phosphine oxide form completely prevails. This tendency has been clearly seen by ^{31}P NMR spectroscopy, whose chemical shifts and ^{31}P-^{1}H couplings revealed that with the exception of the perfluorinated phosphine in Figure 1, all other SPOs exist exclusively in the pentavalent form. Indeed, uncoordinated phosphinous acids have only been described with extremely electron-withdrawing substituents.[20,21]

Montchamp and Janesko[18] have suggested an explanation of this behaviour taking into account an additional resonance form in the prototropic tautomerism of SPOs (Scheme 3).



Scheme 3. Tautomerism and resonance forms of SPOs.

The phosphonium form depicted in Scheme 3 is destabilized by strong electron-withdrawing substituents. But this simple description allows the rationalization of other minor tendencies such as the influence of the solvent in the tautomerism.[19]

It is noteworthy to mention the work of Martin, Buono and co-workers[22] in the assessment of the electronic properties of SPOs. They concluded that the coordinated phosphinous acids are less donating than the corresponding trisubstituted phosphorus

analogues, including not only tertiary phosphines, but also phosphites and aminophosphines. In contrast, deprotonated phosphinous acids (phosphinito ligands)[12] showed strong electron-donating behaviour, being among the most electron-rich P ligands, close to phosphonium ylides, and even surpassing the *N*-heterocyclic carbenes.[12,22]

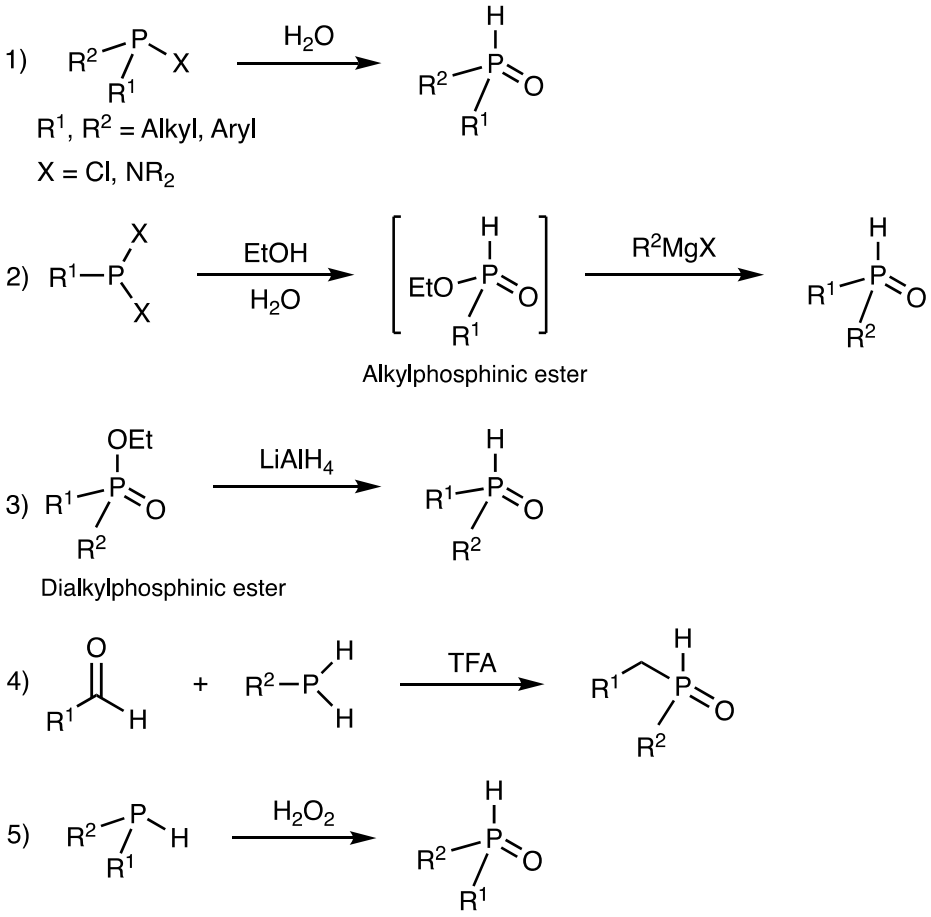
The clear stereoelectronic differences between the neutral coordinated phosphinous acids and their anionic forms are a crucial factor for the exceptional behaviour of these ligands in some catalytic transformations, in which the abstraction of the OH proton occurs during the reaction.

Interestingly it has to be mentioned that in the case of *P*-stereogenic secondary phosphine oxides, the tautomeric equilibrium does not affect the stereochemical integrity of the phosphorus atom[7,16,23] but, despite that, very few optically pure *P*-stereogenic SPOs have been prepared.

3. Synthesis of SPOs

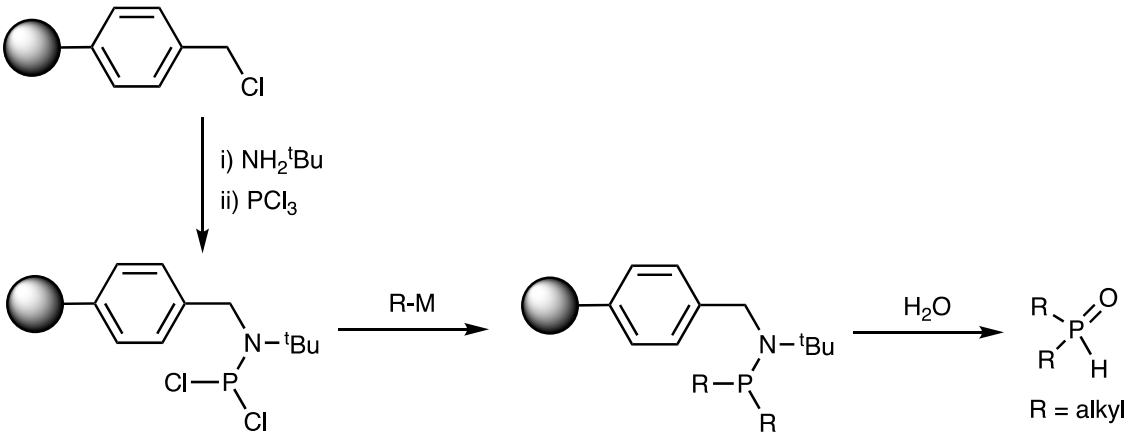
3.1. Achiral or racemic SPOs

Traditionally, SPOs have been classically prepared by the easy hydrolysis of phosphine halides (Scheme 4, 1).[24] Other widely used methodologies are the displacement of an alkoxide from a monosubstituted phosphinic ester by a Grignard reagent (Scheme 4, 2) or by the reduction of a disubstituted phosphinic ester by treatment of lithium aluminium hydride (Scheme 4, 3).[15,25] Condensation of aldehydes with primary phosphines (Scheme 4, 4) also leads to the corresponding SPOs in refluxing trifluoroacetic acid.[26] In addition, the obvious way to prepare SPOs is through oxidation of secondary phosphines with hydrogen peroxide (Scheme 4, 5) or molecular oxygen at 50–70 ºC.[27] This method, however, is rarely employed because it usually produces undesired oxidised byproducts.



Scheme 4. Main synthetic strategies to prepare SPOs.

All these strategies allow the preparation of a variety of SPOs, especially containing aryl substituents.[28] In contrast, dialkyl-substituted secondary phosphine oxides are more difficult to prepare because due to their basicity they undergo non-desired secondary reactions involving the formation of P–O–P bonds. Li and co-workers[29] have reported a useful polymer-supported synthesis of dialkyl substituted SPOs,[29] depicted in Scheme 5.

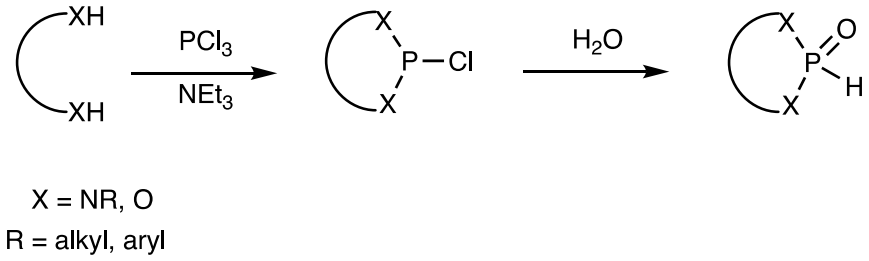


Scheme 5. Polymer-supported synthesis of dialkyl-substituted secondary phosphine oxides.

The polymer-supported aminophosphines can be straightforwardly prepared by treating Merrifield's resin with excess of *tert*-butylamine to form the polymer-supported secondary amine. This resin reacts with PCl_3 in the presence of triethylamine to give the supported dichlorophosphine precursor. Reaction of this precursor with a variety of organolithium and Grignard reagents leads to complete substitution of P–Cl bonds. Finally, the desired SPOs can be obtained by hydrolysis that cleaves the SPO from the resin.[30,31]

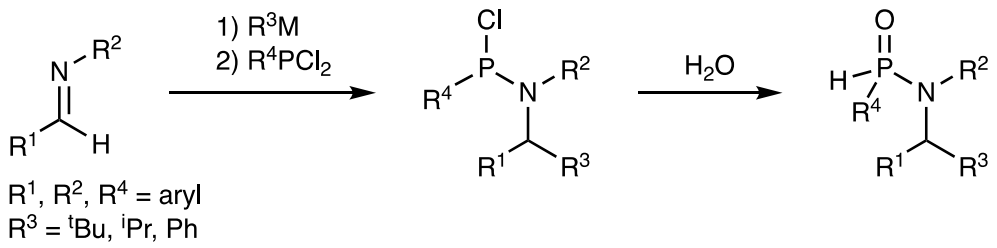
This methodology has been extended to the preparation of bidentate systems by introducing 1,2-bis(dichlorophosphanyl)ethane instead of phosphorus trichloride.[29]

In contrast, (HA)SPOs, *H*-phosphonates or their derivatives, can be directly obtained from the corresponding diamines, diols or aminoalcohols and PCl_3 in a one-pot or two-step procedure (Scheme 6).[32,33]



Scheme 6. General methodology for the preparation of (HA)SPOs.

Other strategies have been developed in order to prepare HASPOs containing P–N bonds. A recent methodology, reported by Hong and co-workers,[34] is based on the reaction of imines with organolithium or Grignard reagents followed by the condensation with a chlorophosphine. The subsequent aqueous work-up of the chloroaminophosphines leads to the desired amino-substituted SPOs (Scheme 7).

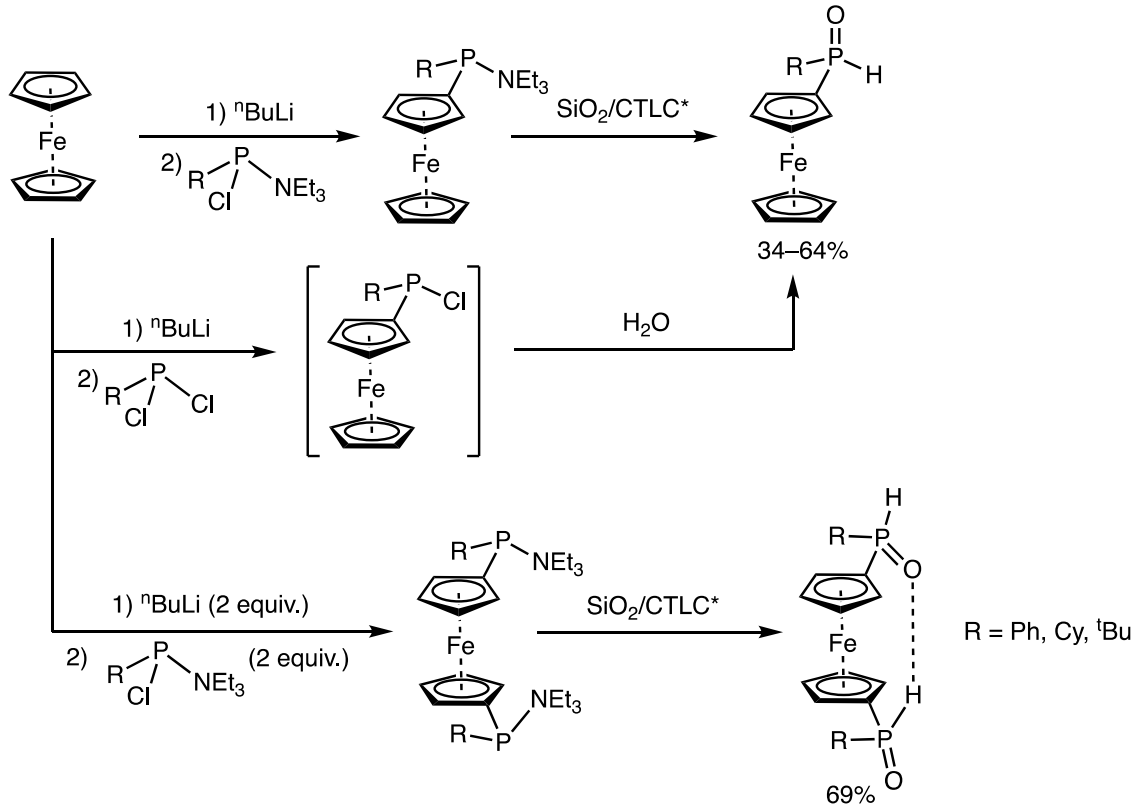


Scheme 7. Preparation of amino-substituted SPOs.

Both procedures provide an attractive platform for the synthesis of enantiomerically enriched secondary phosphine oxides, since the backbone of the diamine or diol, along

with the substituents of the imine, may contain stereogenic elements, as it is discussed in the next section.

The ferrocenyl group has given many interesting ligands and SPOs are not an exception. As an example, Scheme 8 shows the synthesis of a family of ligands described by Hong and coworkers.[35] The ligands were prepared by lithiation of ferrocene, followed by phosphination and hydrolysis and were employed in Pd-catalysed Suzuki-Miyaura couplings.

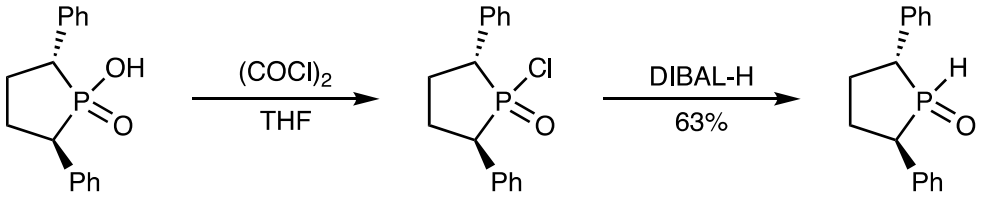


Scheme 8. Synthesis of racemic SPOs bearing a ferrocenyl group. *CTLC = centrifugal thin layer chromatography.

3.2. Non-racemic SPOs

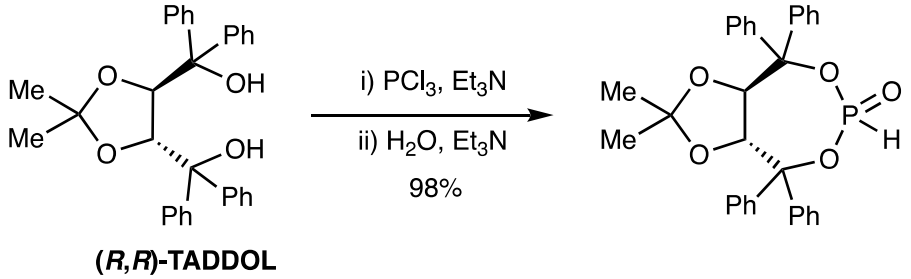
Chiral, non-racemic SPOs can be classified into two broad categories: those that are chiral due to the backbone and *P*-stereogenic SPOs.

The first example of a SPO with a chiral scaffold was described in 1999 by Fiaud and co-workers[36-38] (Scheme 9) and was prepared by diastereomeric resolution using quinine as resolving agent.



Scheme 9. Synthesis of the optically pure diphenylphospholane SPO.

The general method of Scheme 6 employs diamines or diols and inexpensive PX_3 precursors. An interesting asymmetric version of this method was reported in 2000 by Enders and co-workers,[39] making use of the enantiomerically enriched TADDOL[39] (Scheme 10). Several HASPOs have been prepared according to this general synthetic strategy and most of them have proved to be valuable ligands in nucleophilic catalysis.[40,41]



Scheme 10. Synthesis of the (*R*,*R*)–TADDOL-SPO derivative.

In addition, some examples of enantiomerically enriched HASPOs[42] have been obtained from the corresponding optically pure 1,2-diamines (Figure 2).

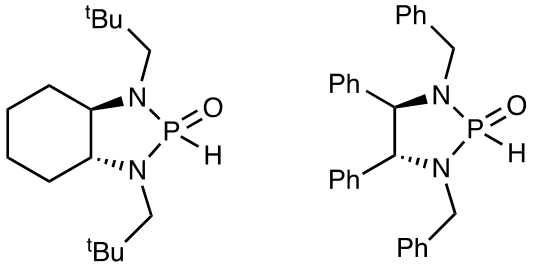
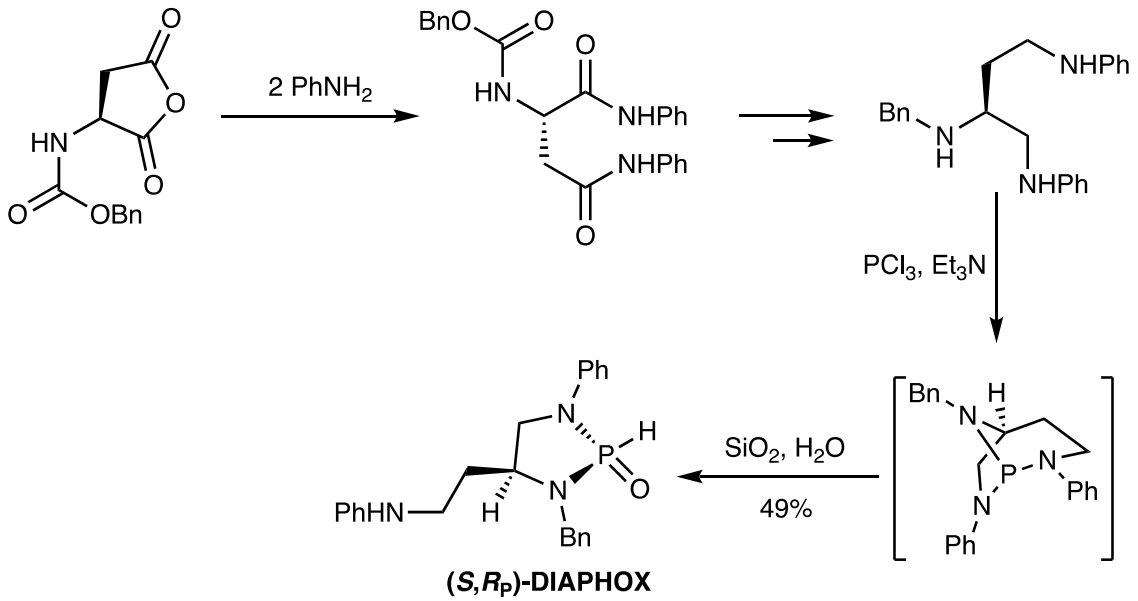


Figure 2. Selected chiral secondary diaminophosphine oxides.

As it can be seen, all the examples presented contain at least one stereogenic element in the backbone. An elegant synthesis of a HASPO with an stereogenic phosphorus atom was reported by Hamada and co-workers (Scheme 11).[10,43-45] In this methodology, L-aspartic acid was converted in a few steps into a chiral triamine. A diastereoselective formation of the corresponding triaminophosphine using PCl_3, followed by the subsequent hydrolysis yielded the desired diaminophosphine oxide

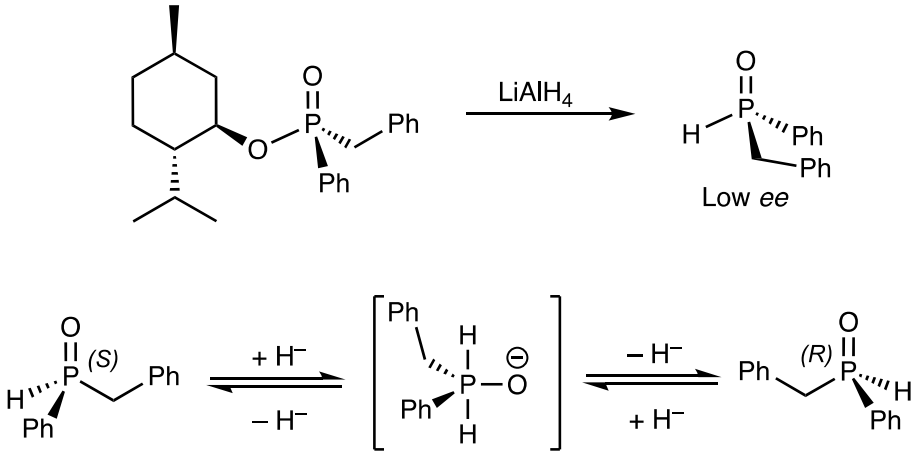
(DIAPHOX). The last step can be considered a S_N2 reaction, which can be easily achieved through column chromatography with wet silica. It is important to note that these special types of ligands have displayed excellent results in many palladium- and iridium-catalysed asymmetric processes providing high enantiomeric excesses, especially in asymmetric allylic substitution reactions.[43,45-49]



Scheme 11. Synthesis of the (S,R_P)-DIAPHOX ligand.

Even though the preparation of SPOs with a chiral backbone is well-established,[42] the same statement is not true regarding *P*-stereogenic SPOs and for this reason only a few examples are known so far.[8,50]

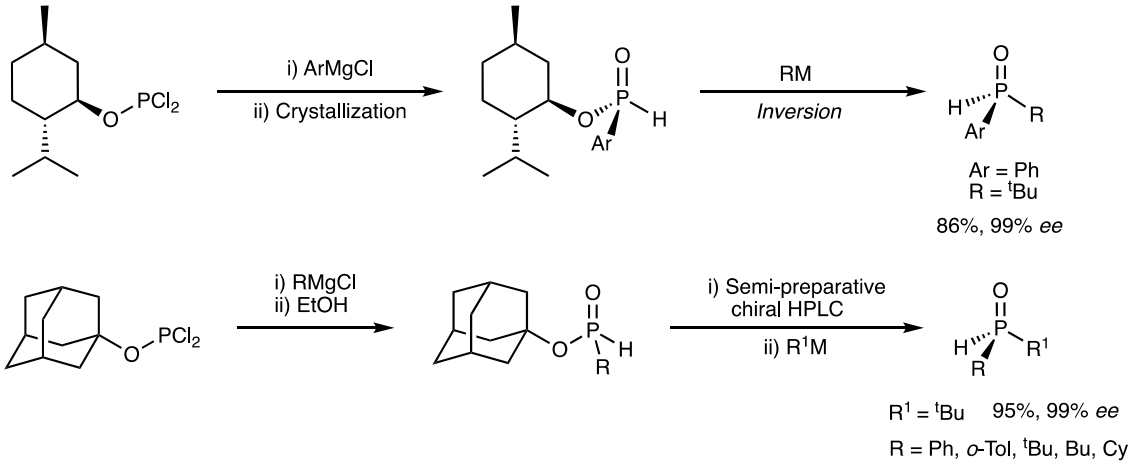
The use of menthylphosphinates as chiral auxiliaries in the preparation of *P*-stereogenic SPOs is relatively well developed.[51] The first synthesis of a *P*-stereogenic SPO was reported in 1968,[15] when benzylphenylphosphine oxide was prepared by reduction of the corresponding menthol-precursor with lithium aluminium hydride (Scheme 12).



Scheme 12. Preparation of the first *P*-stereogenic SPO and its epimerisation.

Mislow and co-workers,[25] however, demonstrated that this method does not constitute a suitable strategy for the preparation of SPOs, since it causes racemization.[25] The epimerization of the phosphorus atom can be rationalised by means of a hydride-addition-elimination mechanism involving a pentacoordinated dihydrido species.

In order to overcome these difficulties, Buono and co-workers[52,53] developed another synthetic route, which relies on the reaction of diastereomerically pure menthyl or adamantyl phosphinate precursors with organolithium and Grignard reagents (Scheme 13). Replacement of the phosphinate moiety occurs with the expected inversion at the phosphorus atom.[54]

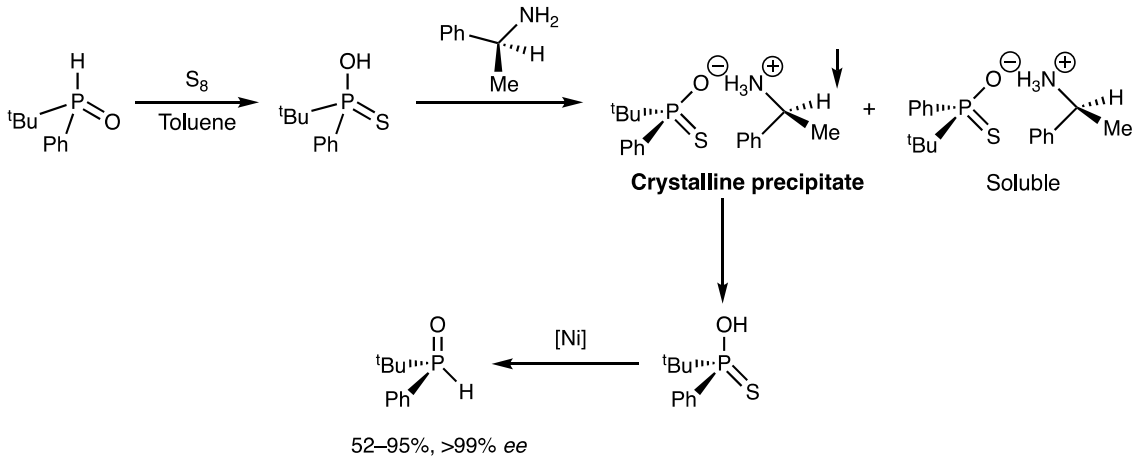


Scheme 13. Asymmetric synthesis of SPOs with organometallic reagents.

Although the substitution reaction works very well for menthylphosphinates (Scheme 13, top)[55] the obtention of optically pure menthylphosphinates is cumbersome when Ar is different from the usual phenyl group. For this reason, enantiopure adamantylphosphinates, obtained by means of expensive semi-preparative HPLC,[56]

were employed (Scheme 13, bottom). In addition, the steric hindrance of the organolithium and Grignard reagents and its excess in the reaction media affect dramatically both the yield and the stereochemical purity of the obtained SPOs. More recently, similar results have been obtained using α-D-glucosamine as a chiral precursor[57] with *ee* values comparable to those reported by Buono and co-workers.[56]

Tert-butylphenylphosphine oxide has traditionally been the most studied *P*-stereogenic SPO. It can be obtained in optically pure form using 1-phenylethylamine as resolving agent,[58,59] in a method that starts with the conversion of the racemic SPO into the corresponding phosphanylthioic acid. Resolution of the phosphanylthioic acid with an enantiomerically enriched amine and subsequent desulfurization in the presence of Raney nickel[58] provides the desired optically pure SPO (Scheme 14).



Scheme 14. Preparation of the optically pure *tert*-butylphenylphosphine oxide by resolution.

Other efficient methods to separate *rac*-^{t}BuPhP(O)H have been described using (*S*)-mandelic acid or ephedrine as resolving agents.[60-62] In parallel, Minnaard and co-workers[63,64] described an elegant dynamic resolution of ^{t}BuPhP(O)H by crystallisation with (–)-dibenzoyltartaric acid, achieving excellent *ee*'s.

Complementary to the above-mentioned methodologies, Feringa, de Vries and co-workers have successfully resolved various SPOs through preparative chiral HPLC.[36,65,66] This technique has allowed the isolation of several enantiomerically enriched SPOs (Figure 3).

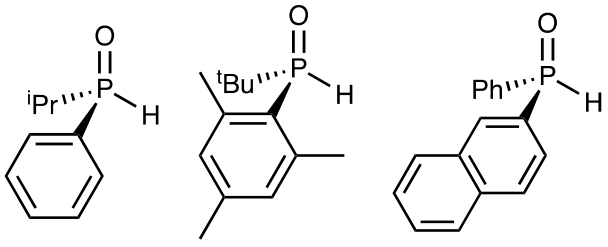
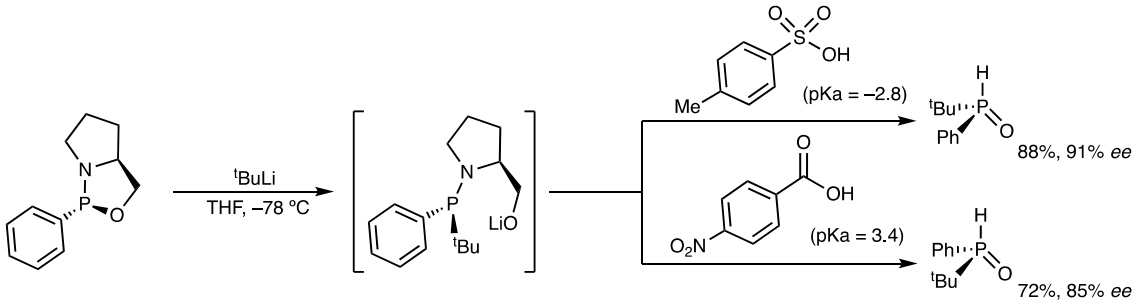


Figure 3. Enantiomerically enriched SPOs through preparative chiral HPLC.

Other strategies for the preparation of optically pure *tert*-butylphenylphosphine oxide via asymmetric synthesis were published in 2005 by Buono and co-workers.[54] In that work they described for the first time, the synthesis of the two enantiomers of ^{t}BuPhP(O)H using an oxazaphospholidine precursor derived from (*S*)-prolinol. The highly diastereoselective ring-opening of the oxazaphospholidine with *tert*-butyllitium in THF at low temperature (Scheme 15) constitutes the key step of the methodology.

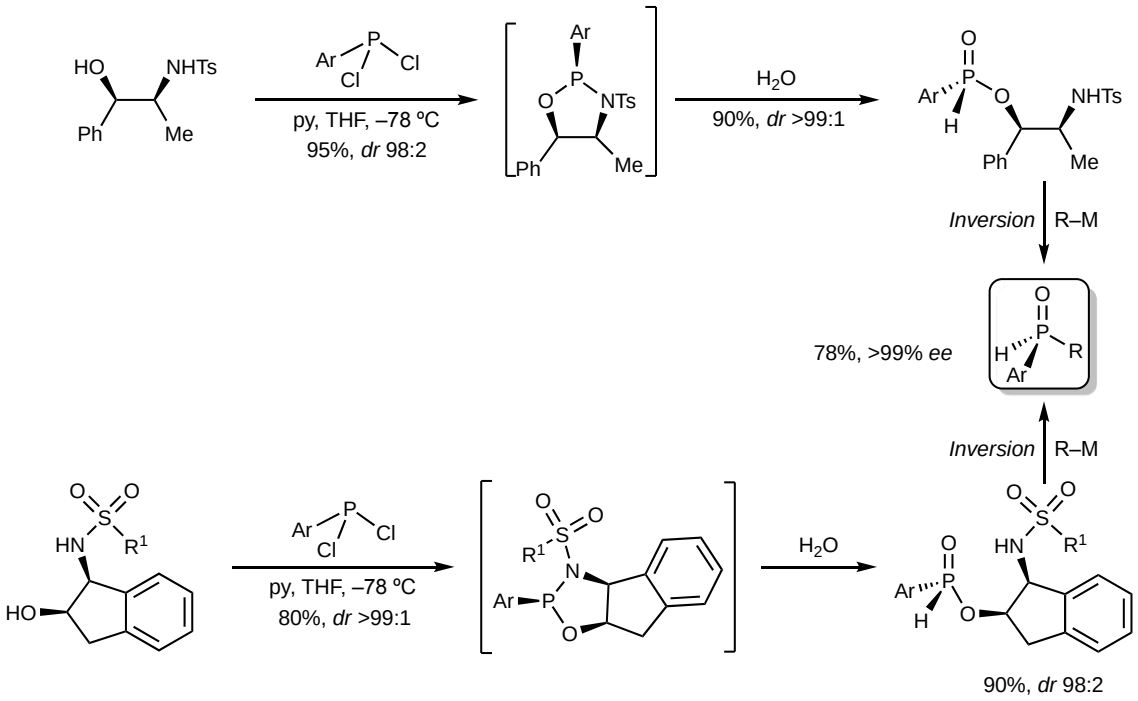


Scheme 15. Synthesis of both enantiomers of ^{t}BuPhP(O)H.

While this ring-opening reaction was shown to proceed with retention of the phosphorus configuration, the obtention of the two enantiomers of the SPO can be accomplished by just changing the Brønsted acid during work-up. Therefore strong Brønsted acids ($pK_a \leq 1$) lead to retention of configuration at phosphorus whereas weaker acids ($pK_a \approx 3–5$) produce products with inversion. Unfortunately, this elegant strategy could not be extended to other SPOs different from ^{t}BuPhP(O)H.

Other approaches have been examined in order to introduce more than one stereogenic element in the structure of SPOs. Dubrovina, Börner and co-workers[9,67] prepared a mixture of diastereomeric dodecahydrodibenzophosphole 5-oxides.[9,67]

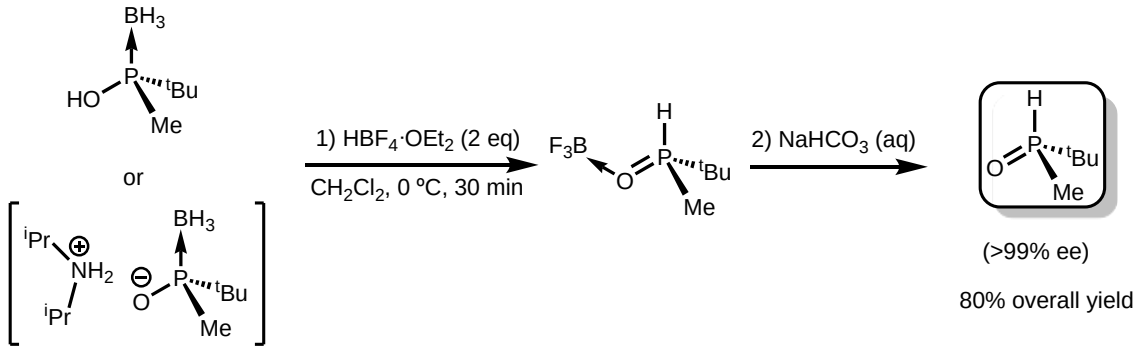
In the search of a general method to prepare chiral SPOs from cheap precursors Han and co-workers[68] have described the use of aminoalcohols as chiral auxiliaries, in particular for SPOs containing naphthyl-derived substituents in combination with bulky groups (Scheme 16).



Scheme 16. Enantioselective synthesis of chiral SPOs employing aminoalcohols.

This example emphasizes the potential use of aminoalcohols as chiral auxiliaries for the preparation of *P*-stereogenic SPOs, even though this methodology is, in fact, more general and can be extended to the synthesis of many *P*-stereogenic ligands.

Very recently, our group designed for the first time the synthesis of enantiopure (*S*)-^{t}BuMeP(O)H using enantioselective synthesis (Scheme 17).[69]



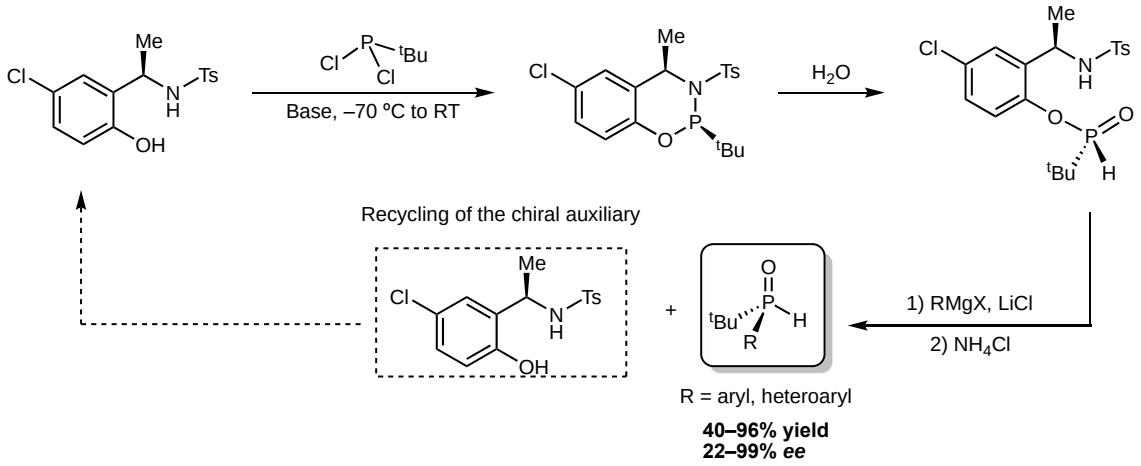
Scheme 17. Synthesis of **(*S*)-**^{t}BuMeP(O)H. Its enantiomer has been prepared analogously.

The phosphinous acid-borane precursor was prepared by hydrolysis of the corresponding amino derivative.[70,71] Since the synthesis starts from *cis*-aminoindanol,[70] both enantiomers are equally accessible.

Treatment of the phosphinous acid-borane with tetrafluoroboric acid [62,72] affords the boron trifluoride adduct of the desired compound as a stable solid. This adduct constitutes the second reported crystal structure of a SPO–BF_3 adduct after a

phospholane oxide–BF_3 adduct reported by Toffano and co-workers.[73] Analysis of the crystal structure supports that the mechanism of deboronation[74] takes place by substitution of the hydrogen atoms of the borane group by fluorine, as suggested by McKinstry and co-workers.[75] After basic hydrolysis the desired oxide was obtained as in high yield and excellent enantioselectivity.

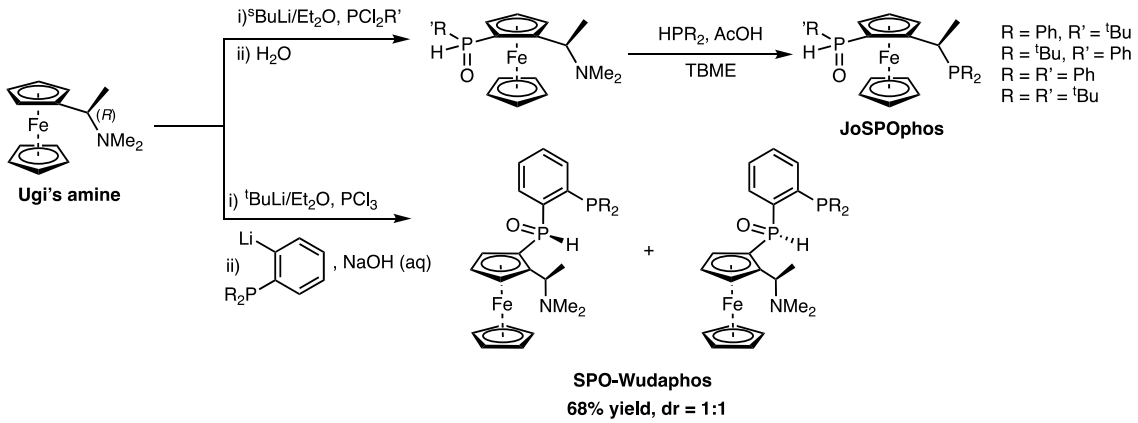
Very recently, Senanayake and Tsantrizos[76] reported the synthesis of a library of SPOs bearing the *tert*-butyl group, also using a chiral aminoalcohol as chiral auxiliary (Scheme 18).



Scheme 18. Synthesis of *t*-butyl containing *P*-stereogenic SPOs.

The synthesis was based on the formation of a *P*-stereogenic *H*-phosphinate by condensation of *t*-$BuPCl_2$ with the chiral aminoalcohol, followed by hydrolysis. Nucleophilic displacement of the auxiliary by Grignard reagents and hydrolysis provided a library of *P*-stereogenic SPOs. The synthesis is interesting because avoids the use of highly pyrophoric reagents such as *t*-BuLi to make the synthesis more amenable for large scale preparations of ligands.

There are also several optically pure ligands bearing the ferrocenyl substituent that deserve to be mentioned, since they produced excellent hydrogenation catalysts. Pugin, Pfaltz and coworkers[77] some time ago described mixed phosphine oxide-phosphine ligands with a ferrocenyl substituent, called JoSPOphos, because were reminiscent of Josiphos (Scheme 19). These ligands had a stereogenic phosphorus atom and a chiral backbone and were obtained from the well-known of Ugi's amine. Recently Berthold and Breit have reported new JoSPOphos ligands.[78]

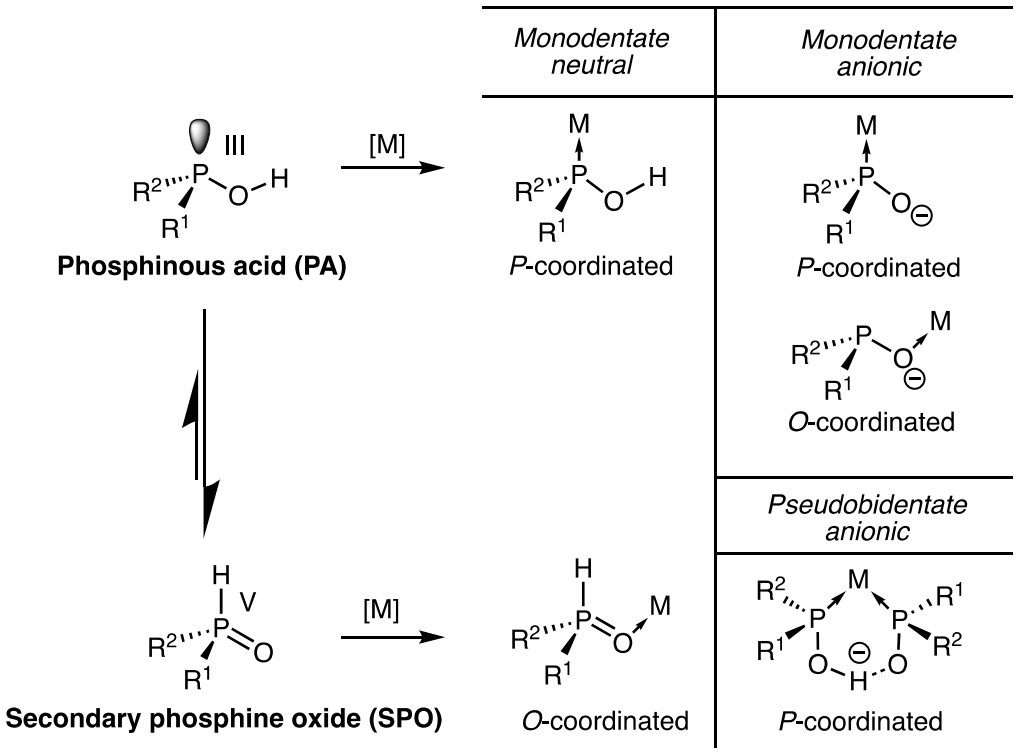


Scheme 19. Preparation of JoSPOphos and SPO-Wudaphos ligands.

In another approach, Chung, Dong, Zhang and coworkers,[79,80] inspired by the properties of enzymes, designed a special type of SPOs (called SPO-Wudaphos), also starting from Ugi's amine (Scheme 19). These ligands were designed to engage ion pair and H-bond noncovalent interactions for highly enantioselective asymmetric hydrogenations of several substrates.

4. Complexation of SPOs

Secondary phosphine oxides can act, as neutral species, as ambidentate ligands by using the *soft* phosphorus atom in the PA tautomer or the *hard* oxygen atom in the SPO tautomer (Scheme 20).[81,82]



Scheme 20. Tautomeric equilibrium PA-SPO and main coordination modes of SPOs.

The coordinative behaviour depends, among other factors, on the affinity of the metal for one site or the other. In general, early transition metals coordinate through the hard oxygen atom, giving M–SPO complexes, and the late transition metals (more employed in homogeneous catalysis) through the soft phosphorus atom, producing M–PA complexes.[11,83,84] Hence, examples of *P*-coordinated complexes can be found for Fe, Pd, Ir, Au, Pt, Rh and Ru whereas the *O*-coordination has been described for example with Ti, Cr, Mo, W, Mn, Re and Ru among others. Interestingly, for some cations in the same oxidation state examples of both types of coordination are found in the literature, such as the complexes of Scheme 24 and Scheme 25. This shows how subtle are the factors that influence the coordination of one ore another tautomer. It has to be noted, however, that in the vast majority of the complexes used in catalysis the *P*-coordination of SPOs (as PAs) predominates. Despite this, in the literature these metallic systems are usually called complexes with “SPO ligands” when strictly speaking they should be named as complexes with “PA ligands”. In the present review, the usual nomenclature is usually employed except when emphasis on the PA tautomer is intended.

PAs are weak acid that can be easily deprotonated by bases.[85] This originates anionic, very electron-donating *phosphinito* ligands, which again can generate either *P*-coordinated or *O*-coordinated complexes (Scheme 20). Examples of the more common

former kind of complexes include Mo, W, Mn, Re, Fe, Pt and Au while the latter coordination has been found for Fe, Rh, Ir and Ag.[11]

A recent review by Igau and his coworker[12] deals with the complexes of anionic, *P*-coordinated phosphinito (also called "phosphoryl") ligands ($M–P(O)R^1R^2$), some of which may surpass carbenes in terms of electronic donation. They are interesting ligands not only in catalysis but also in supramolecular chemistry since they are strong hydrogen bond acceptors. Of course, $M–P(O)R^1R^2$ can considered complexes with SPO ligands (although they are very often not prepared by coordinating the SPO to the metallic precursor)[12] and therefore some of them and their catalytic applications are discussed in the present review. However, full account of their synthesis, properties and applications is not given and can be conveniently found in the mentioned review.[12]

Interestingly, two SPO units attached to a metal centre can form an intramolecular hydrogen bond, acting as an anionic pseudobidentate ligand (Scheme 20). This moiety can be formally considered as assembled by combination of a neutral phosphinous acid and an anionic phosphinito unit. This process often requires an external base and leads to a stable six-membered ring. Although the formation of such species is both thermodynamically and kinetically favoured, the required *cis* geometry can not always be achieved and sometimes the *trans* isomers with two monodentate PAs are obtained instead.[22,69,81] Nevertheless, this pseudobidentate coordination mode has spurred interest into the study of the applications of SPOs in catalysis[7,11] and it has been found, for example, that dialkyl SPOs are excellent ligands for cross-coupling reactions.[6]

It is interesting to note that sometimes the phosphinous acid ligand can be modified during the catalysis, such as in the allylic alkylation,[86] in which the OH group is silylated by *N,O*-bis(trimethylsilyl)acetamide (BSA) and therefore it is no longer a "true" phosphinous acid.

Finally it has to be mentioned that SPOs are being increasingly used in the stabilisation of nanoparticles (NPs).[87] One of the earliest reports in this direction was the observation of Wang and Buhro,[88] who noted that dioctylphosphine impurities had a profound impact on the morphology of CdSe nanocrystals. Inspired by this result several SPO-stabilised metallic nanoparticles have been synthesised and are being tested in catalytic reactions, as will be discussed in the present review.

4.1. Ruthenium

Although the first examples of Ru systems bearing PO–H···PO bridges were initially published during the 1980's,[89-91] it was not until 1999 when these studies were extended to SPOs[92] (Figure 4).

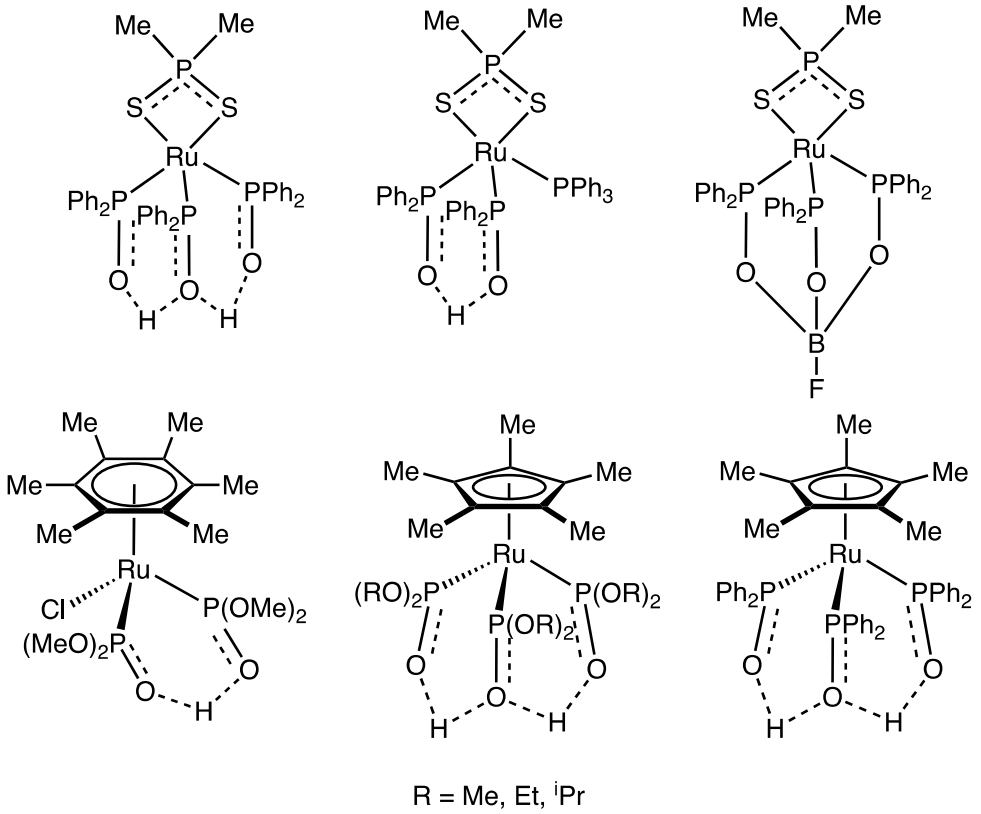
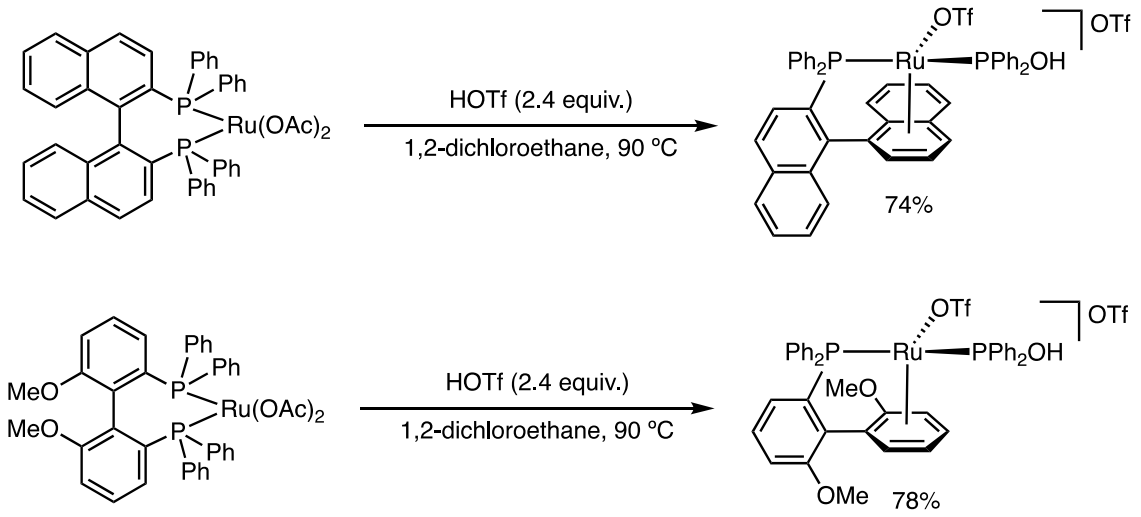


Figure 4. Ru complexes containing PO–H···PO bridges.

Ru(II) compounds containing the dimethyldithiophosphinate ligand were discovered by Robertson, Stephenson and co-workers[89] while they were studying the reactivity of PPh_2Cl with *cis*-$[Ru(S_2PMe_2)_2(PPh_3)_2]$. Refluxing such complex in a mixture of acetone and water allowed the obtention of compounds depicted in Figure 4. The intermolecular H-bridges could be successfully substituted, forming a chelate, upon treatment of the pseudobidentate complexes with $BF_3{\cdot}Et_2O$.

Hexamethylbenzene Ru(II) complex could be straightforwardly prepared, with good yield reacting the hexamethylbenzene ruthenium(II) dimer in refluxing methanol and 4 equivalents of $(MeO)_2P(O)H$.[90] In contrast, Koelle and co-workers[91] prepared the trisubstituted complexes $[RuCp^*\{(PPh_2O)_3H_2\}]$ and $[RuCp^*\{(P(OR)_2)_3H_2\}]$ upon treatment of the Ru(II) dimer $[\{RuCp^*(\mu\text{-OMe})\}_2]$ with $Ph_2P(O)H$ or $(RO)_2P(O)H$. These compounds contain two PPh_2OH units and a PPh_2O^- connected by hydrogen bond interactions (Figure 4).

Almost at the same time Ru(II) complexes with atropoisomeric biaryl-SPOs were also described (Scheme 21).[93-95]



Scheme 21. Preparation of tethered (η^6–arene)-Ru(II) complexes by hydrolysis of phosphorus-carbon bonds.

The synthesis of these aryl triflate ruthenium(II) complexes was carried out reacting an excess of not thoroughly dry triflic acid with a solution of the Ru(II) acetate precursor in 1,2-dichloroethane. In this reaction, the triflic acid protonates the acetate and a water molecule splits the P–C bond as described by Pregosin and co-workers.[96]

Although the preparation of Ru(II)-tethered complexes is a well-known topic[97-101] it is noteworthy to mention the especial reactivity of phosphinous acid Ru(II)-tethered complexes, because treatment with HBF_4 affords chelate-complexes, similarly to those described with O–BF_2–O bridges (Figure 5).

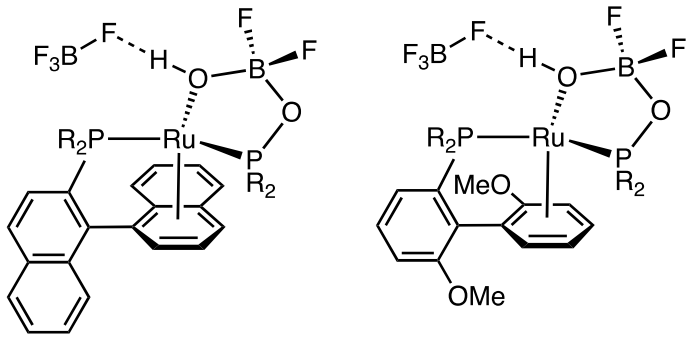


Figure 5. Tethered (η^6–arene)-ruthenium(II) complexes containing O–BF_2–O bridges.

The first attempts to prepare *piano-stool* ruthenium(II) structures containing P–OH bonds, in order to achieve a pseudobidentate ligation, were described with P(OMe) substituents[102] and no catalytic applications were found for these complexes until the work of Ackermann,[103] in which they used electron-rich SPOs in ruthenium-catalysed arylation reactions between pyridines or imines and aryl chlorides.

At present the number of phosphinous acid Ru(II)-arene type complexes is considerably high.[13] Their synthesis usually takes place by scission of dimers [RuCl(μ-Cl)(η^6-arene)]$_2$ (for arene = *p*-cymene, mesitylene and hexamethylbenzene, among others) with two equivalents of the corresponding SPO or HASPO (Figure 6).

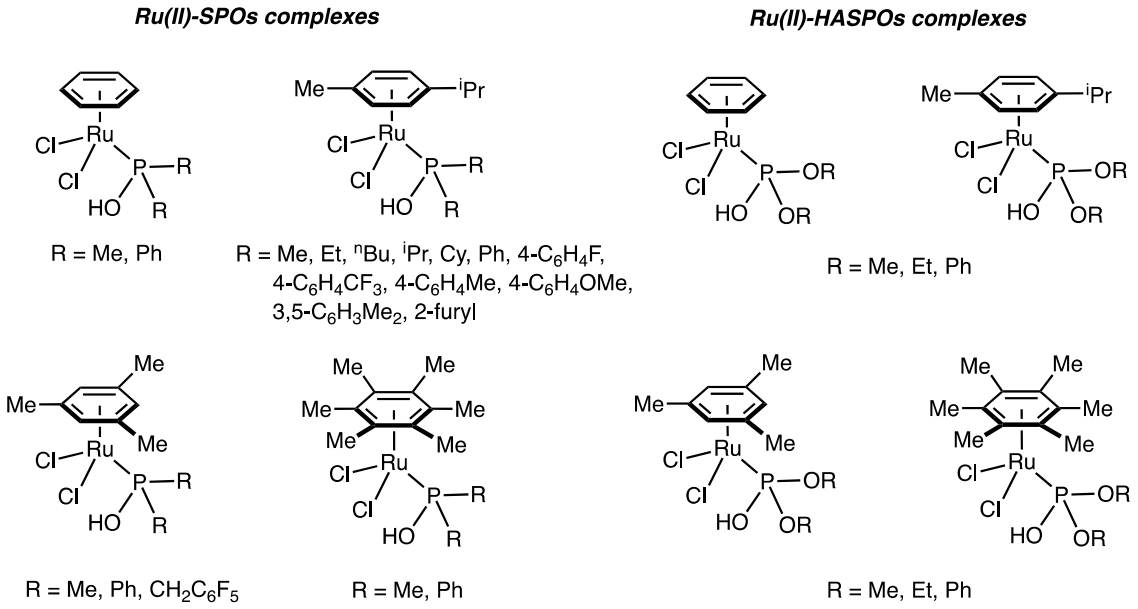
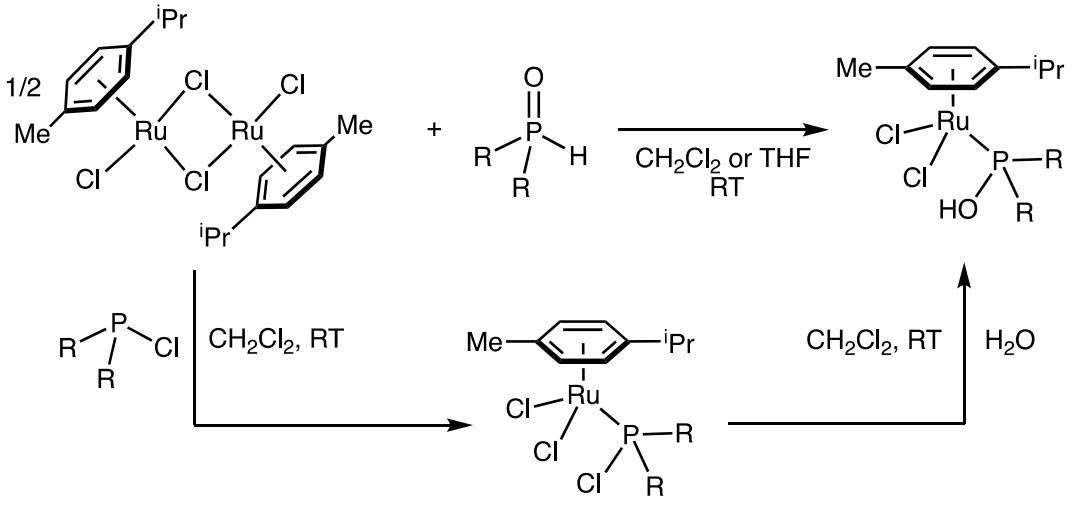


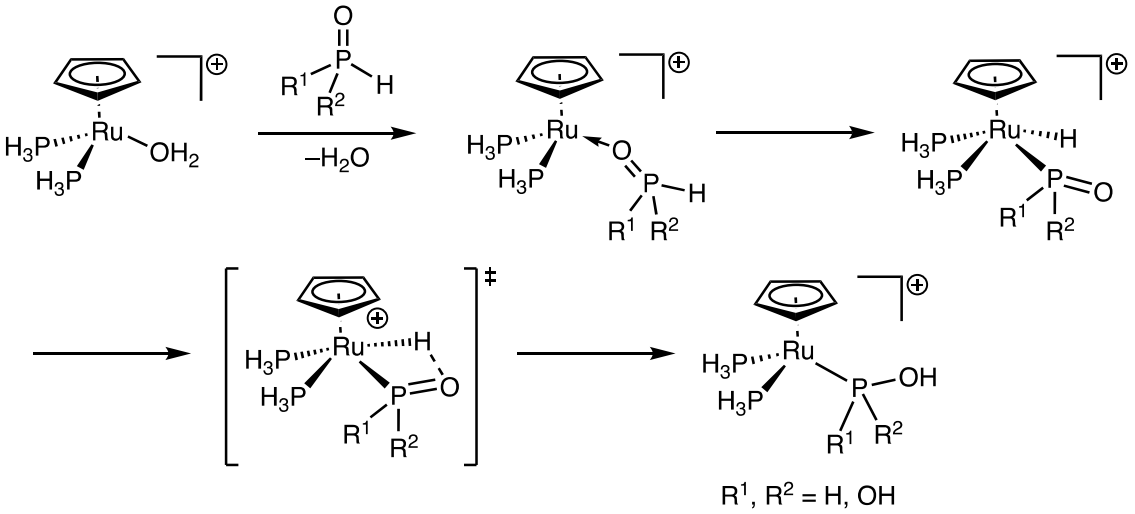
Figure 6. *Piano-stool* Ru(II)-PA complexes.[104-107]

These reactions are known to take place due to the tautomerism of the (HA)SPOs, followed by the cleavage of the chloride bridges to afford the corresponding mononuclear complexes. However, another synthetic strategy relies on the coordination of a chlorophosphine precursor to the coordination sphere of Ru(II) and later hydrolysis to afford the desired compounds, as described by Cadierno and co-workers.[105,107]



Scheme 22. Preparation of Ru(II)-*p*-cymene SPO complexes.

From a mechanistic point of view this process appears to be slightly more complex, as it has been demonstrated by Peruzzini, Mealli and co-workers[108] in the tautomerism and coordination of compounds $H_nP(O)(OH)_{3-n}$ with $[RuCp(PH_3)_2(OH_2)]^+$ fragments. Hence, according to DFT studies the lowest reaction energy barriers are found for a reaction pathway in which the ligand is initially *O*-coordinated as a SPO. This coordination mode allows a later rearrangement to the *P*-coordinated compound, a PA (Scheme 23).



Scheme 23. Calculated reaction pathway for the formation of complexes $[RuCp(PH_3)_2(SPO)]^+$.

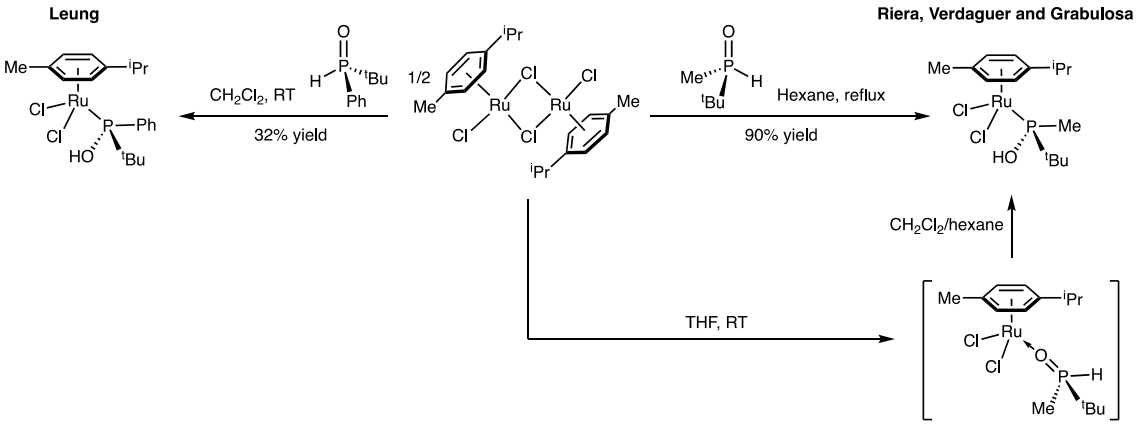
The direct transfer of a P-bound H atom to the terminal oxo oxygen (1,2-proton shift) by a purely acid-base process is energetically prohibitive by the uncoordinated SPO, due to the high covalency of the P–H bond. The metal assisted tautomerisation is much easier and in the studied case occurs via a four-legged piano stool Ru hydride species, formed by oxidative addition of the SPO. From this intermediate the H ligand is transferred to the phosphoryl group.

A related behaviour can be also observed in the coordination of some SPOs to Ru(II) arene systems, where the *O*-coordinated analogue is detected in solution and tautomerises upon precipitation.[69,106]

The use of optically pure SPOs as ligands in asymmetric catalysis is quite scarce, and when it comes to Ru(II) systems, the only precedent was described by Leung and co-workers[102] in the coordination of optically pure (*S*)-^{t}BuPhP(O)H.

Therefore, and due to the growing interest in catalysis of the more soluble Ru(II)-*p*-cymene complexes, compared to other arenes, we envisaged in our group the preparation of the optically pure Ru(II) complex containing (*R*)-^{t}BuMeP(O)H, following

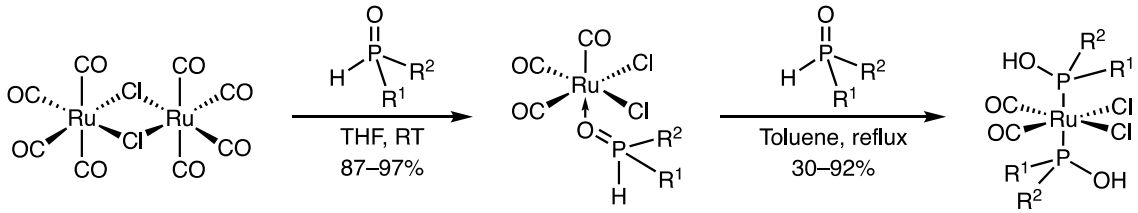
the procedures described by Ackermann and co-workers[109] and by Buono and co-workers[106] as it is depicted in Scheme 24.



Scheme 24. Preparation of Ru(II)-*p*-cymene-SPO complexes.

In our studies it was possible to detect the formation of *O*-coordinated species, reacting the dimer with a slight excess of (*R*)-^{t}BuMeP(O)H. Interestingly, when we tried to isolate this species by precipitation with hexane, only the *P*-coordinated complex was obtained in low yield. In order to improve the yield, the reaction was carried out in refluxing hexane.[109] It turned out that with this procedure the desired complex was obtained in high yield despite the insolubility of the Ru dimer in this solvent.

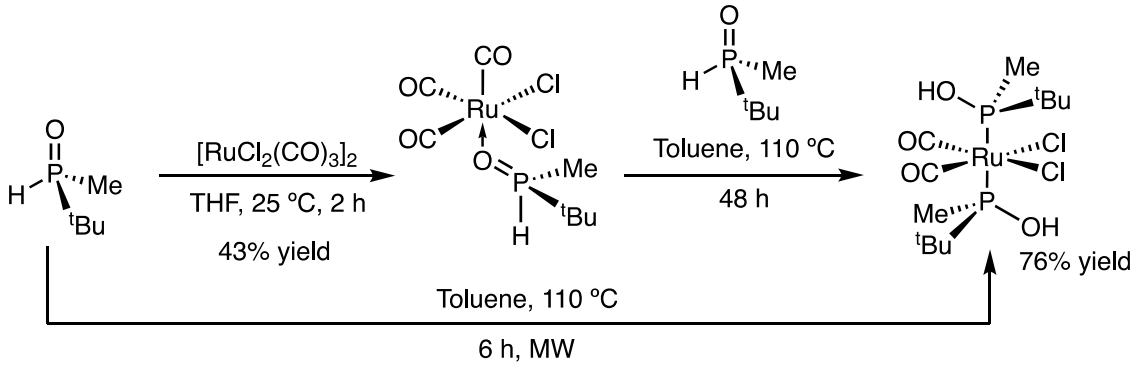
The coordination of bulky and basic phosphinous acids has been found to be difficult because of the lack of stability of the complexes formed. It is known, however, that electron-withdrawing ligands such as arylphosphines or carbonyl groups tend to facilitate the introduction of more than one SPO in the coordination sphere. This behaviour has ben also observed for Ru by Buono and co-workers,[81] who reported the synthesis of ruthenium carbonyl complexes bearing SPOs (Scheme 25) which have been successfully applied in the cycloisomerisation of arenynes (Scheme 81).



R^1 = Ph; R^2 = Me, ^{n}Bu, ^{t}Bu, Cy
R^1 = R^2 = Cy, Ph, 4-C_6H_4F

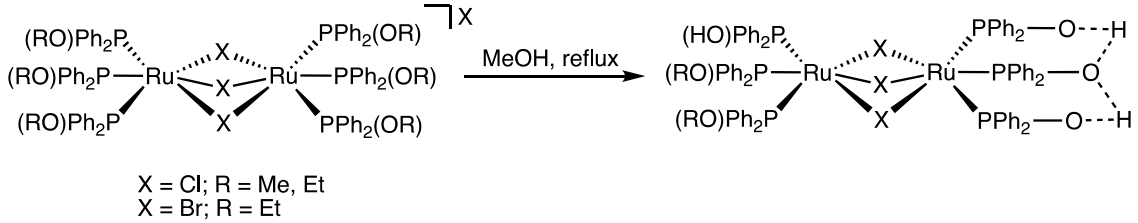
Scheme 25. Preparation of bis-coordinated Ru(II)-SPO complexes.

Our own efforts in the area[69] led to the isolation of both *O*- and *P*-coordinated complexes following previous methodologies.[81] The treatment of $[RuCl_2(CO)_3]_2$ with (*S*)-^{t}BuMeP(O)H in THF at room temperature yielded the *O*-coordinated complex as a stable solid (Scheme 26). Treatment of this complex with another equivalent of (*S*)-^{t}BuMeP(O)H in toluene at 110 ºC for two days produced the bis-coordinated compound, albeit with low yield. In order to find a more convenient method, the reaction was carried out under microwave conditions, which led to a higher yield in much shorter time affording the desired complexes with stereochemical retention at phosphorus.



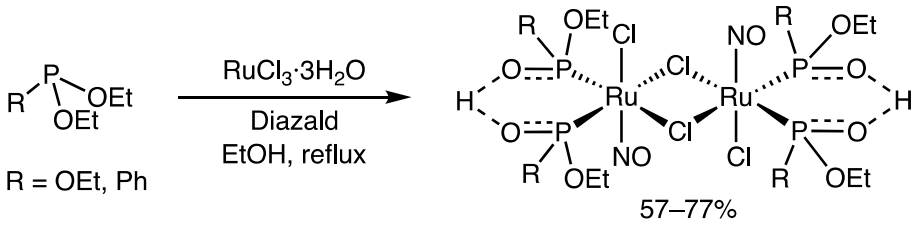
Scheme 26. Synthesis of optically pure *O*- and *P*-coordinated Ru(II) complexes.

The preparation of Ru(II) dinuclear derivatives was initially disclosed by Gould, Stephenson and co-workers,[110] who described trihalide-bridged Ru(II) complexes by hydrolytic cleavage of the coordinated phosphinites into phosphinous acid derivatives, connected by intramolecular hydrogen-bridges (Scheme 27). Hydrolysis of the phosphinite ligands is thought to occur due to the presence of water in the methanol solutions.



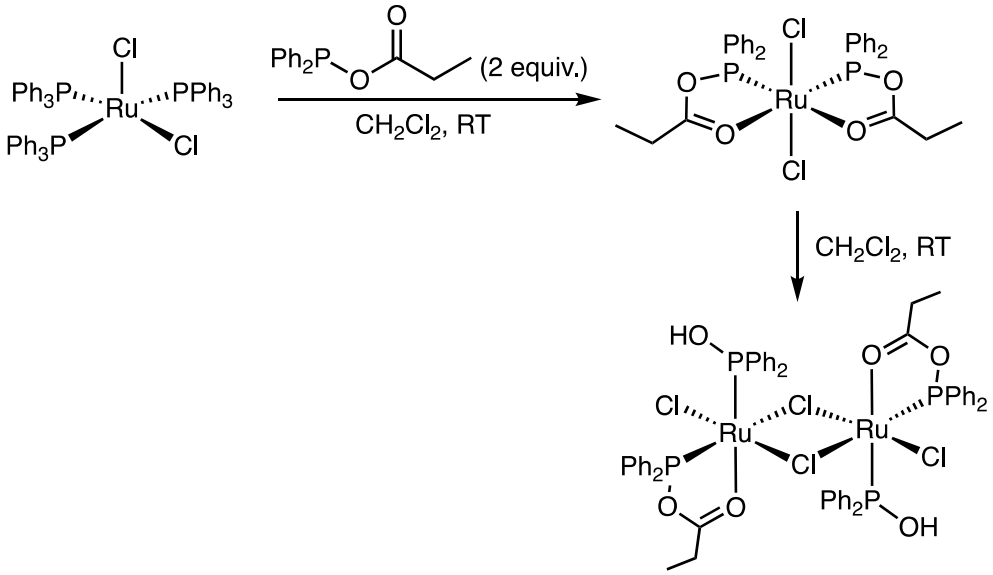
Scheme 27. Preparation of Ru(II) dinuclear complexes containing intramolecular H-bonds.

Nitrosyl-ruthenium(II) dimers forming pseudobidentate architectures have been also described,[111] by reaction of $RuCl_3$ with the corresponding $P(O)R(OEt)_2$ derivatives and diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) as a nitrosating agent (Scheme 28).



Scheme 28. Preparation of pseudobidentate Ru(II) dinuclear complexes.

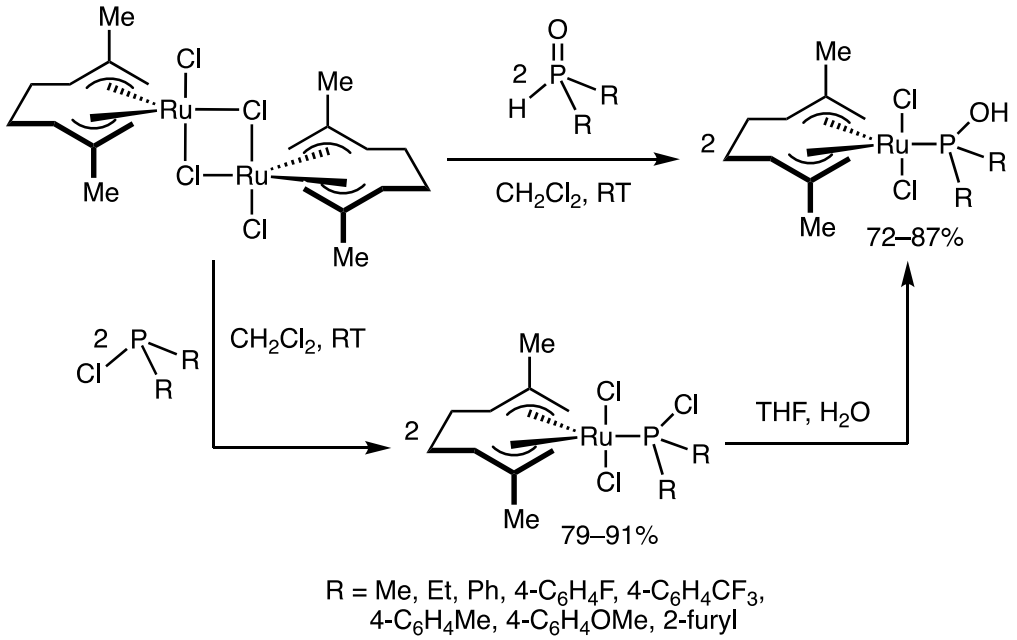
Another interesting dinuclear Ru(II) was described by Cole-Hamilton and coworkers[112] by reaction of $[RuCl_2(PPh_3)_3]$ and two equivalents of a mixed anhydride-phosphinite ligand (Scheme 29).



Scheme 29. Preparation of a dinuclear Ru(II) complex.

This complex, whose structure was elucidated by X-ray diffraction methods, was formed by a rearrangement reaction of the mixed anhydride ligand, as it happens with Rh(III) (Scheme 40).

There are some examples in the literature of phosphinous acid complexes containing Ru centres in other oxidation states. In this regard, it is noteworthy to mention the works of Cadierno and co-workers[113,114] in the preparation of Ru(IV)-bis(allyl)-SPO complexes (Scheme 30).



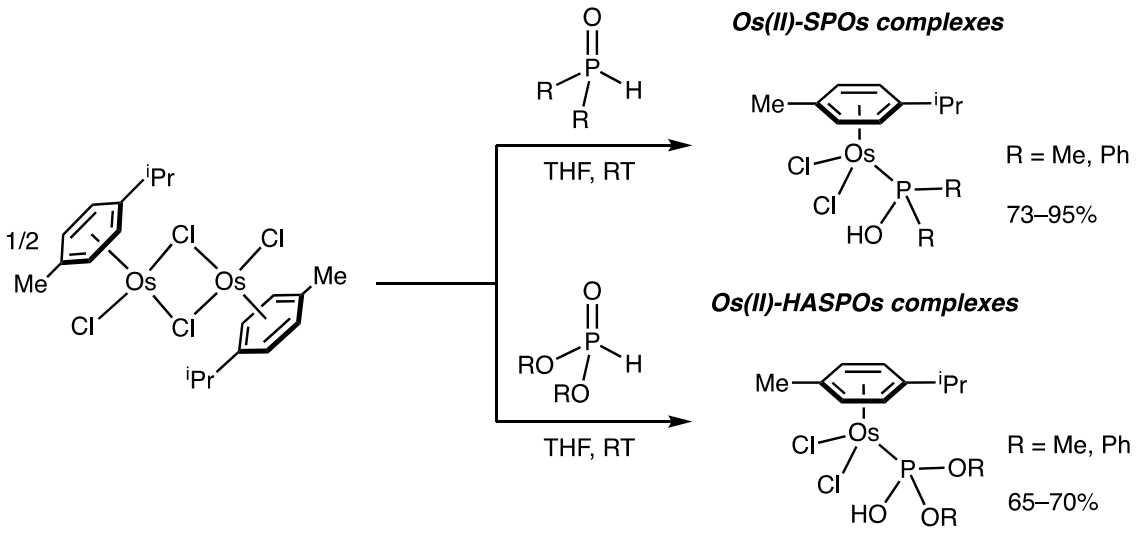
Scheme 30. Preparation of bis(allyl)-ruthenium(IV)-SPO complexes reported by Cadierno and co-workers.[113,114]

These complexes were straightforwardly prepared by direct reaction of several alkyl and aryl SPOs with the chloride-bridged dimeric precursor in dichloromethane. Those complexes containing aromatic SPO units could be also prepared by hydrolysis of the chlorophosphines in THF/H_2O mixtures.

As a closing remark to the Ru complexes with SPO ligands it has to be noted that Yakhvarov, Peruzzini and coworkers[115] were able to generate the simple but extremely unstable phosphine oxide (H_3PO) electrochemically and stabilise its tautomer (phosphinous acid, $H_2P(OH)$) in the form of a Ru(II)-Cp complex.

4.2. Osmium

Despite its close similarity with ruthenium, much less research has been carried out on osmium complexes with SPO ligands. Cadierno and co-workers[116] have recently described the coordination of phosphinous acids to the $[OsCl_2(\eta^6\text{-}p\text{-cymene})]_2$ dimer forming in moderate to high yields complexes of the type $[OsCl_2(\eta^6\text{-}p\text{-cymene})(PR_2OH)]$ and $[OsCl_2(\eta^6\text{-}p\text{-cymene})\{P(OR)_2OH\}]$ (Scheme 31).

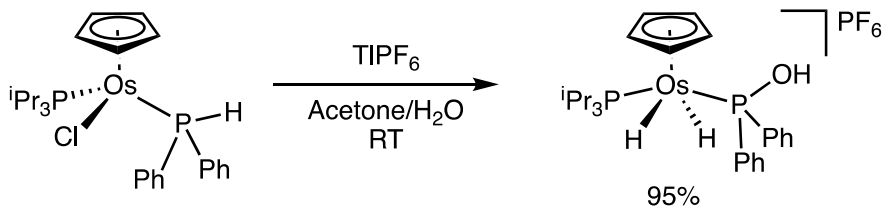


Scheme 31. Preparation of Os(II)–*p*-cymene complexes described by Cadierno and co-workers.[116]

The scission of the Os(II)-*p*-cymene dimer takes place in THF at RT, where the SPO ligands show a clear preference towards the *P*-coordination mode. As observed for analogous Ru(II)-arene complexes, reactions involving phosphites are kinetically slower than those with SPOs.[116]

These Os(II)-arene systems could also be straightforwardly prepared in high yields by hydrolysis of the P–Cl bond in complexes $[OsCl_2(\eta^6\text{-}p\text{-cymene})(PR_2Cl)]$ by reflux in wet THF. Similarly, due to the sluggish reactivity of the related $[OsCl_2(\eta^6\text{-}p\text{-cymene})\{P(OR)_2OH\}]$ complexes, its hydrolysis requires more drastic hydrolytic conditions, a behaviour also observed for the cleavage of the P–N bonds in amino-phosphine derivatives $[OsCl_2(\eta^6\text{-}p\text{-cymene})\{PR_2(NMe_2)\}]$.[116,117]

The reactivity of Os(IV) systems was explored by Esteruelas and coworkers[118] who isolated the cationic complex $[OsH_2Cp(P^iPr_3)(PPh_2OH)]PF_6$ upon reaction of the neutral precursor $[OsClCp(P^iPr_3)(PHPh_2)]$ in the presence of $TlPF_6$ in wet acetone (Scheme 32).

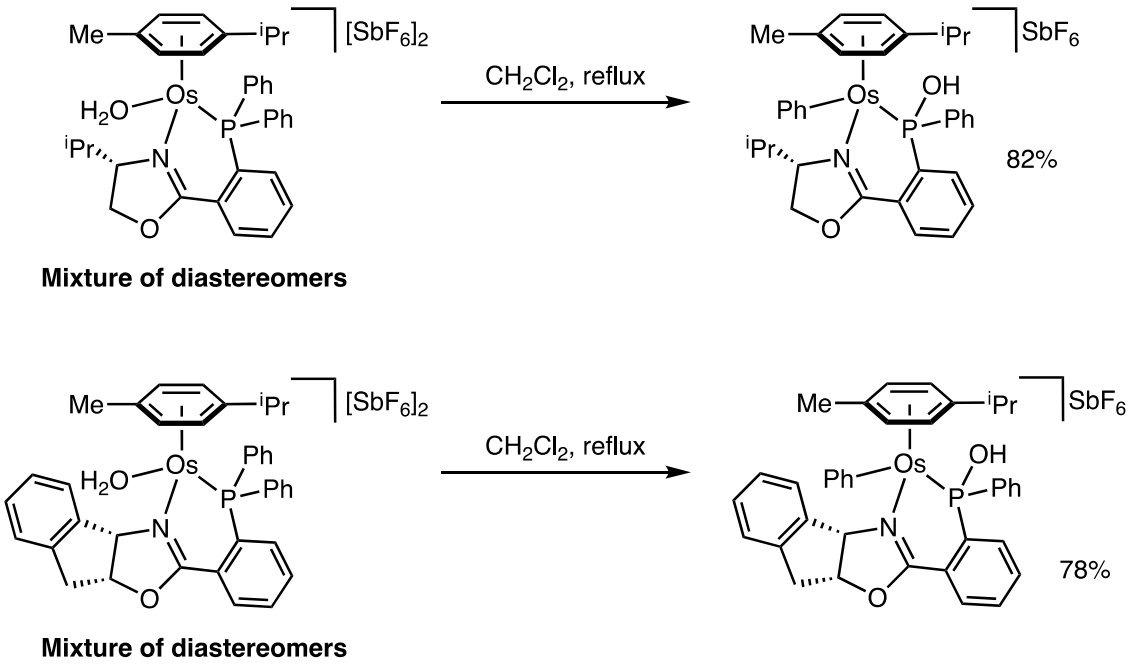


Scheme 32. Synthesis of the diphenylphosphinous acid Os(IV) complex.

The reaction seems to occur by P–H oxidative addition of the diphenylphosphine ligand on the unsaturated intermediate formed upon chloride abstraction with the Tl(I) salt.

Further addition of a water molecule to the Os(IV)=PPh_2 moiety affords the complex in high yield. The same procedure has been successfully applied to the preparation of pentahydride-diphenylphosphine Os(IV) complexes and the detected intermediates support the proposed mechanism.[119]

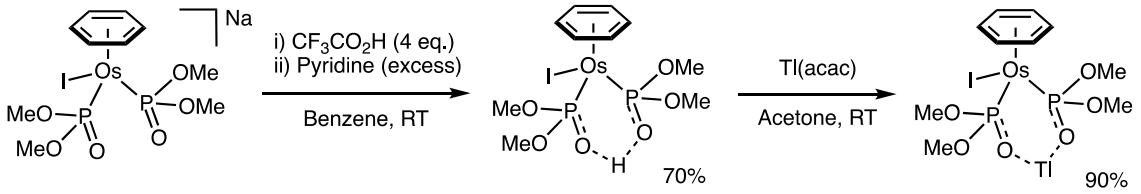
Although other less common oxidation states have been explored in osmium-SPO complexes, such as the porphyrin-Os(VI) derivatives described by Che and co-workers,[120] an increasing interest have appeared in the design of bidentate and pseudobidentate SPO ligands able to coordinate Os(II)-arene fragments. In this line, Carmona and co-workers[121] reported the preparation of *P*,*N*-based Os(II) dicationic aquacomplexes containing optically active phosphinooxazoline ligands (Scheme 33).



Scheme 33. Hydrolytic P–C cleavage in cationic Os(II)-arene complexes.

These compounds appeared as non-separable mixtures of diastereoisomers that were transformed into the related monocationic species in refluxing dichloromethane. Under these conditions one of the Ph groups migrates from the phosphorus to the osmium centre, giving an oxazolino-SPO ligand coordinated.

Another interesting example of a pseudobidentate benzene-Os(II) complex, was prepared by protonation of the bis(dimethylphosphonate) precursor with an excess of trifluoroacetic acid, followed by treatment with an excess of pyridine (Scheme 34). The formation of the heterobimetallic complex can be successfully accomplished reacting the pseudobidentate species with a Tl(I) salt triggering the H^+/Tl^+ exchange.[122]



Scheme 34. Preparation of pseudobidentate Os(II) complexes.

4.3. Rhodium

Although the first application of Rh-SPO complexes was disclosed in the early 1980s for the hydroformylation of linear olefins,[123] a more intense catalytic interest appeared when SPOs were successfully applied to asymmetric hydrogenation of imines[124] and more recently of functionalised olefins.[77] Despite excellent catalytic results, little research about the nature of the Rh species involved in the catalysis has been performed so far.[124,125]

In particular, there are only a few examples of isolated pseudobidentate Rh complexes in the literature containing SPOs with electron-withdrawing substituents (Figure 7).[125,126]

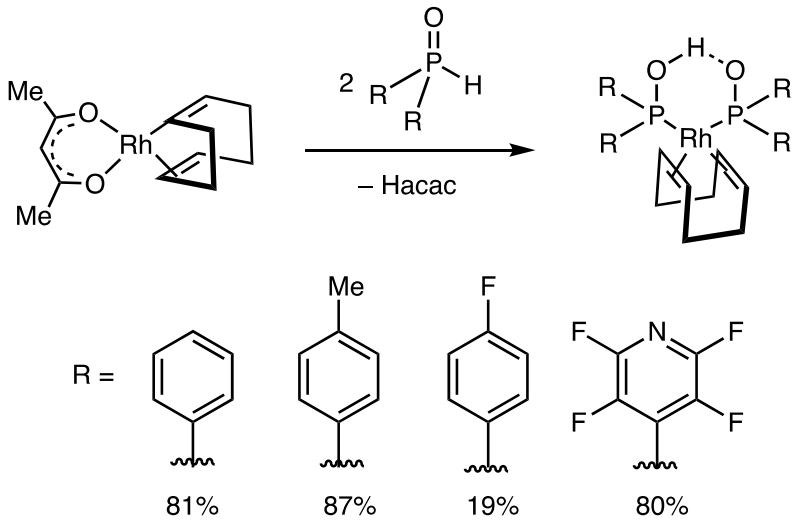
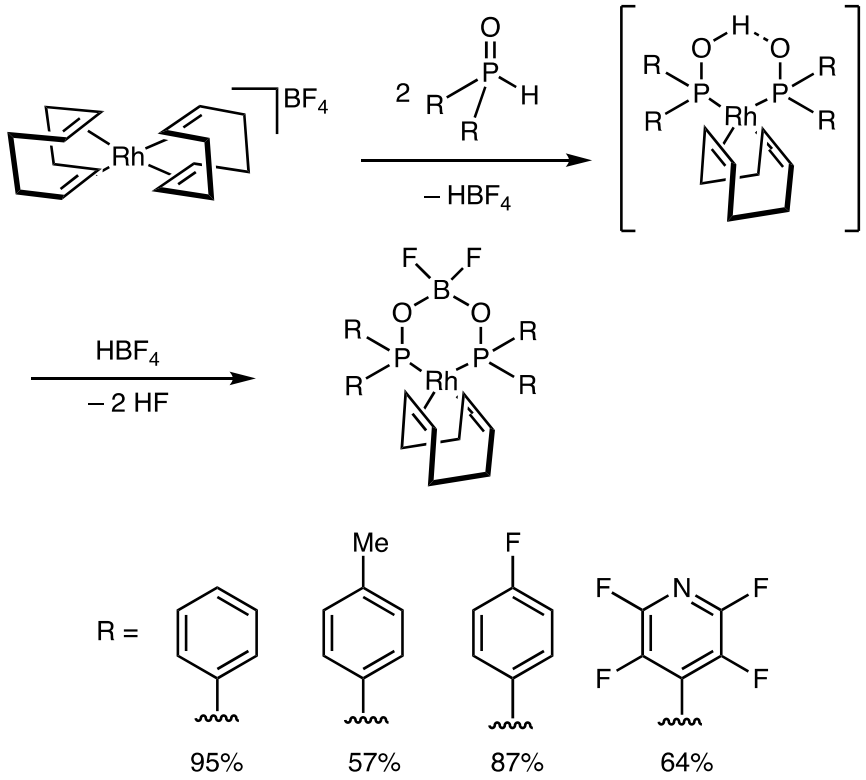


Figure 7. Pseudobidentate Rh complexes reported in the literature.

Börner and co-workers[126] managed to prepare a family of neutral Rh(I) SPO complexes by reaction of two equivalents of ligand with [Rh(acac)(COD)] in THF. The basicity of the acetylacetonate anion is able to deprotonate the OH group, forming the pseudochelated complexes. According to X-ray studies, the shortening of the P–Rh length is correlated with the increase of the electron-withdrawing character of the substituents, as expected. In this line, it is interesting to recall that aryl SPOs tend to react faster with metallic centres, affording more stable complexes. A clear example of

this trend was also discussed by Börner and co-workers.[126] They observed that while the SPO containing the perfluorinated ligand immediately reacted at –78 ºC with Rh, electron-richer di-*tert*-butylphosphine oxide only produced traces of the expected complex, even at elevated temperatures.

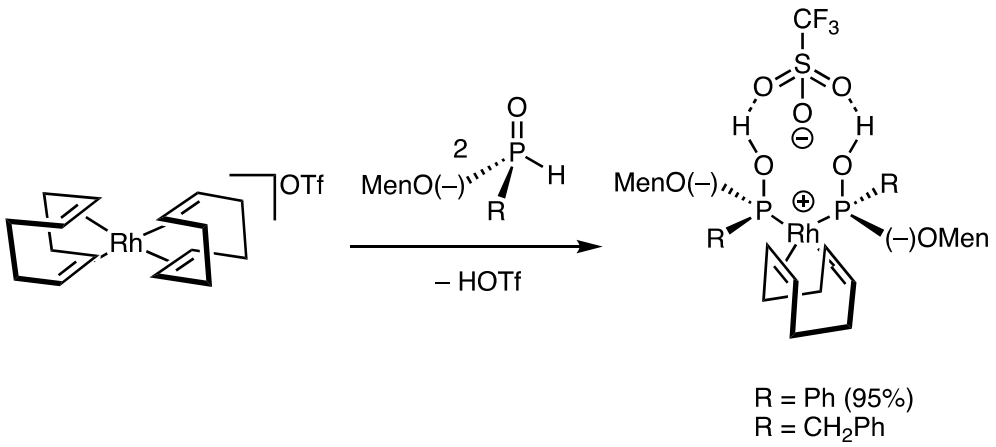
Reactivity of the aryl SPO-Rh(I) pseudobidentate complexes was further studied by Börner's group[126] when they prepared some BF_2–bridged complexes (Scheme 35) formed *in situ* by later chelation with a BF_2 unit.



Scheme 35. Preparation of aryl-SPO Rh(I)–BF_2 capped complexes.

Although reaction of the pseudobidentate complexes with BF_3, $BF_3{\cdot}Et_2O$ and HBF_4 gave only poor yields of the desired complexes[126], the authors circumvented these difficulties reacting 2 equivalents of $[Rh(COD)_2]BF_4$ to directly afford the BF_2–substituted analogues.

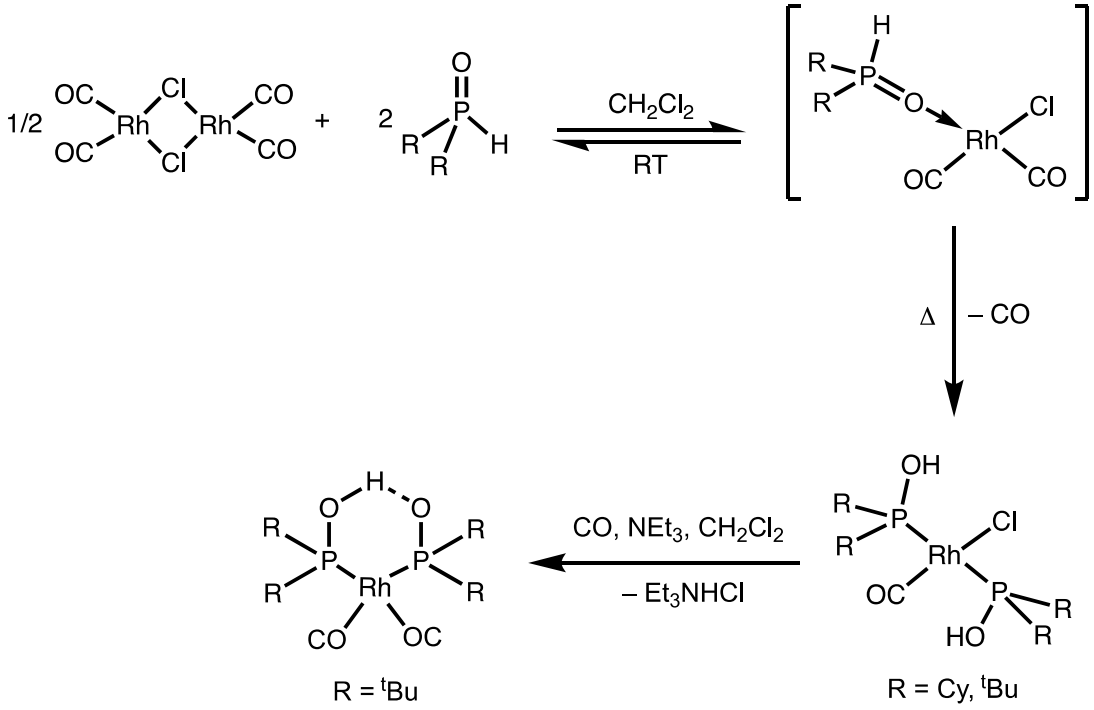
Other examples of formation of bidentate systems were described by Han and co-workers[125] by reaction of the optically pure menthylphenyl- and menthylbenzyl SPOs with $[Rh(COD)_2]OTf$ (Scheme 36).



Scheme 36. Rh complexes prepared by Han and co-workers.[125]

X-ray analysis showed that the two optically pure ligands were linked trough the P atoms in a *cis* fashion as expected, in which the terminal OH units were in turn interacting in a H-bond with the O of the OTfcounterion. Furthermore, the stereochemistry of P was preserved.

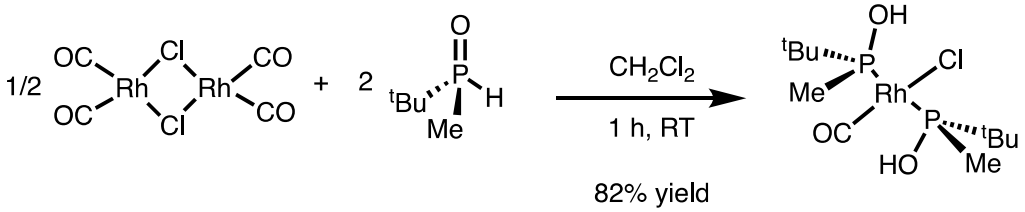
In spite of the difficulties in the isolation of electron-rich SPO-Rh(I) complexes, Martin, Buono and co-workers[22] managed to prepare a Vaska-type complex $[L_2Rh(CO)Cl]$ for L = $(^tBu)_2P(O)H$ and $(Cy)_2P(O)H$ (Scheme 37).



Scheme 37. Synthesis of Rh(I) alkyl-SPO complexes.

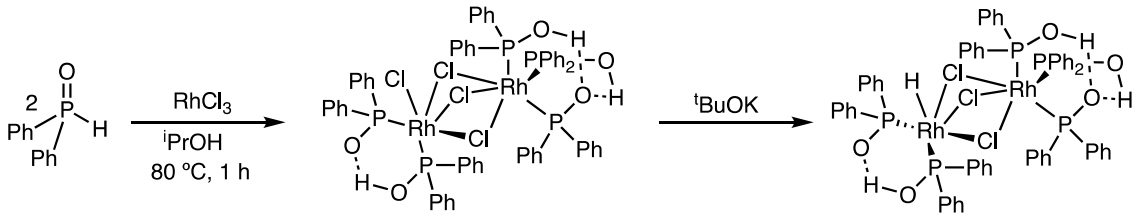
Reaction of $[Rh(CO)_2(\mu\text{-}Cl)]_2$ with two equivalents of the ligand affords the corresponding *O*-coordinated complex, whose formation appears to be reversible, according to ^{31}P NMR spectroscopy. The pseudobidentate Rh(I)complex was prepared by chloride abstraction under CO atmosphere, which isomerises the *trans* complex to the *cis* analogue.

In our group[69] we also studied the reaction of $[Rh(CO)_2(\mu\text{-}Cl)]_2$ with 2 equivalents of the optically pure (*S*)-^{t}BuMeP(O)H in dichloromethane that produced *trans*-[RhClCO((*S*)-^{t}BuMeP(O)H)$_2$] (Scheme 38). The *trans* arrangement of the phosphinous acid ligands was confirmed by NMR spectroscopy.



Scheme 38. Preparation of complex *trans*-[RhClCO((*S*)-^{t}BuMeP(O)H)$_2$].

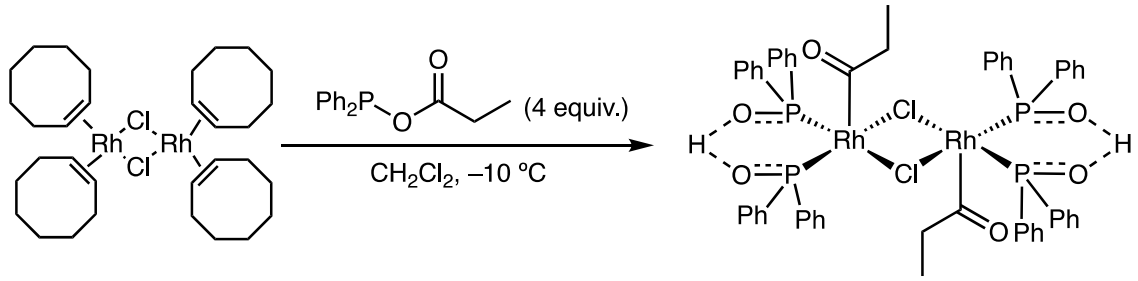
Rh(III)–SPO complexes are rare in the literature. The earliest examples were given by Stephenson, Roundhill and coworkers more than 35 years ago,[127,128] when they isolated triply chloride-bridged Rh(III) dimers with a pseudobidentate diphenylphosphinous acid-diphenylphosphinite ligand by reacting rhodium(I) precursors or rhodium trichloride with several phosphorus compounds in mixtures of simple alcohols and water. Many years later Reid and coworkers[129] reported similar compounds by reaction of rhodium trichloride with diphenylphosphine in ethanol. Much more recently, Van Leeuwen and co-workers[130] revisited and expanded this chemistry by reporting the preparation of a μ-Cl_3 bridged dimeric, octahedral Rh(III) complex bearing the same anionic pseudobidentate ligand (Scheme 39).



Scheme 39. Formation of Rh(III) complexes described by van Leeuwen and co-workers.[130]

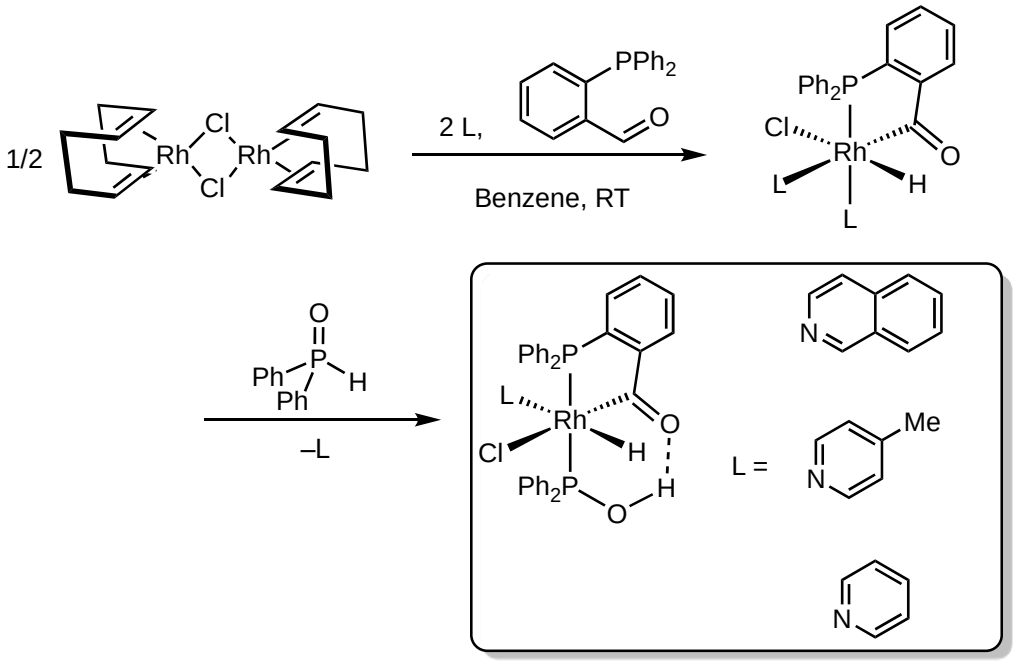
Reaction of the SPO with $RhCl_3$ in refluxing isopropanol afforded the dimeric complex, which can be later treated with *tert*-butoxide forming the Rh hydride. These species have been successfully applied as catalysts for transfer hydrogenation reactions.[130]

In their detailed research on the coordination chemistry and rearrangements of mixed anhydride ligands of the general formulae $R_2POC(O)R'$, Cole-Hamilton and coworkers[112] serendipitously obtained a Rh(III) dimer containing a propanoyl moiety (Scheme 40). This compound was probably produced by the presence of adventitious water in the reaction medium.



Scheme 40. Obtention of Rh(III)SPO-acyl dimer.

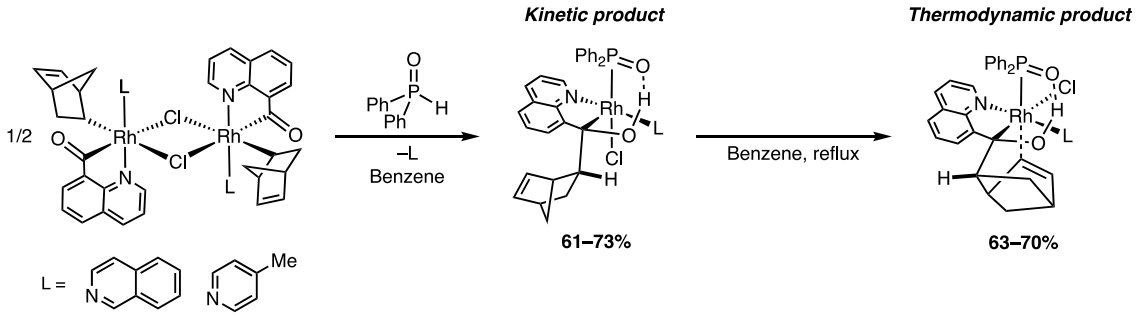
In 2014 Garralda and coworkers[131] reported interesting Rh(III)-acyl complexes with a SPO by reaction of acylrhodium(III) precursors with diphenylphosphinous acid (Scheme 41).



Scheme 41. Preparation of Rh(III)-SPO complexes.

The complexes had a moderately strong intramolecular hydrogen bond between the acyl and the diphenylphosphinous acid. This kind of complexes was employed as homogeneous catalysts in the hydrolysis of ammonia- and amine-boranes to produce hydrogen.

More recently, the same group[132] has reported another type of Rh(III)-SPO complexes by reaction of dimeric Rh(III) species with diphenylphosphinous acid (Scheme 42).

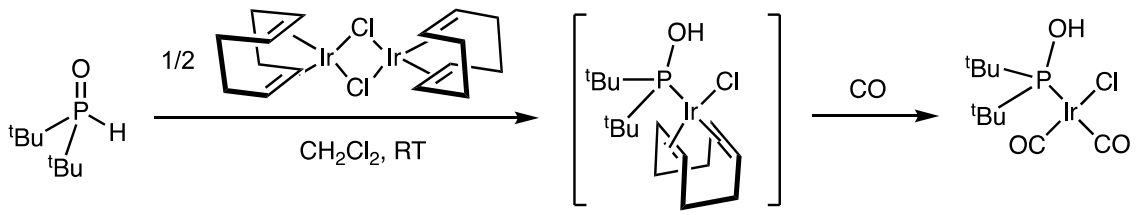


Scheme 42. Preparation of Rh(III)/SPO-acyl complexes.

The addition of diphenylphosphinous acid to saturated acyl-alkyl-Rh(III) complexes led to the formation of a kinetic product that upon heating rearranged to the thermodynamic product, possibly through a Rh(I) intermediates. The mechanism of formation of the complexes were thoroughly studied by theoretical methods because can be relevant for several catalytic transformations.

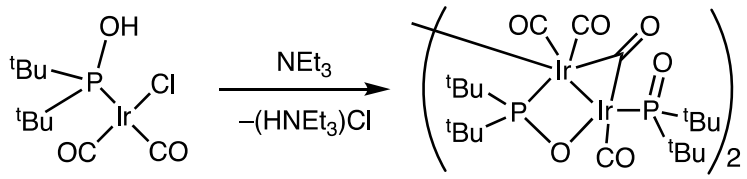
4.4. Iridium

There is an early report of Stephenson and coworkers[127] in which they describe several Ir(III)-SPO complexes. Despite this report, complexation studies with Ir and SPO ligands are rare in the literature, although it has been found that *in situ* prepared Ir precursors with SPO ligands are competent systems for asymmetric hydrogenation of ketimines[66] and functionalized olefins.[124] Indeed, the first preformed Ir(I) complexes described were reported in 2011 by Buono and co-workers[22] using achiral $(^tBu)_2POH$ (Scheme 43). The monocoordinated Ir complex was prepared reacting $(^tBu)_2POH$ with the dimeric iridium precursor. Subsequent treatment of this solution under carbon monoxide atmosphere triggers the substitution of COD by CO. In our group we managed to characterise in solution the analogous Ir complex with the optically pure ligand ^{t}BuMeP(O)H.[69] Attempts to prepare complexes with two of these ligands under the conditions of Martin and co-workers were unsuccessful.[22]



Scheme 43. Reported Ir-SPO complexes with $(^tBu)_2POH$.[22]

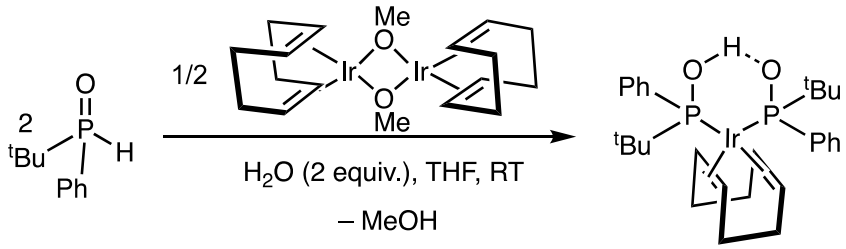
Attempts to deprotonate the coordinated phosphinous acid with triethylamine produced and interesting tetrameric iridium cluster[22] (Scheme 44).



Scheme 44. Deprotonation of an Ir-phosphinous acid complex.[22]

Although this procedure is clearly not a preparative method, it strongly suggests that the presence of a base triggers the formation of polymetallic species, containing Ir–Ir bonds.

More recently, van Leeuwen and co-workers[133] have been able to prepare, for the first time, a bis-coordinated iridium(I) complex containing two ^{t}BuPhP(O)H units forming a pseudobidentate H-bridge (Scheme 45).

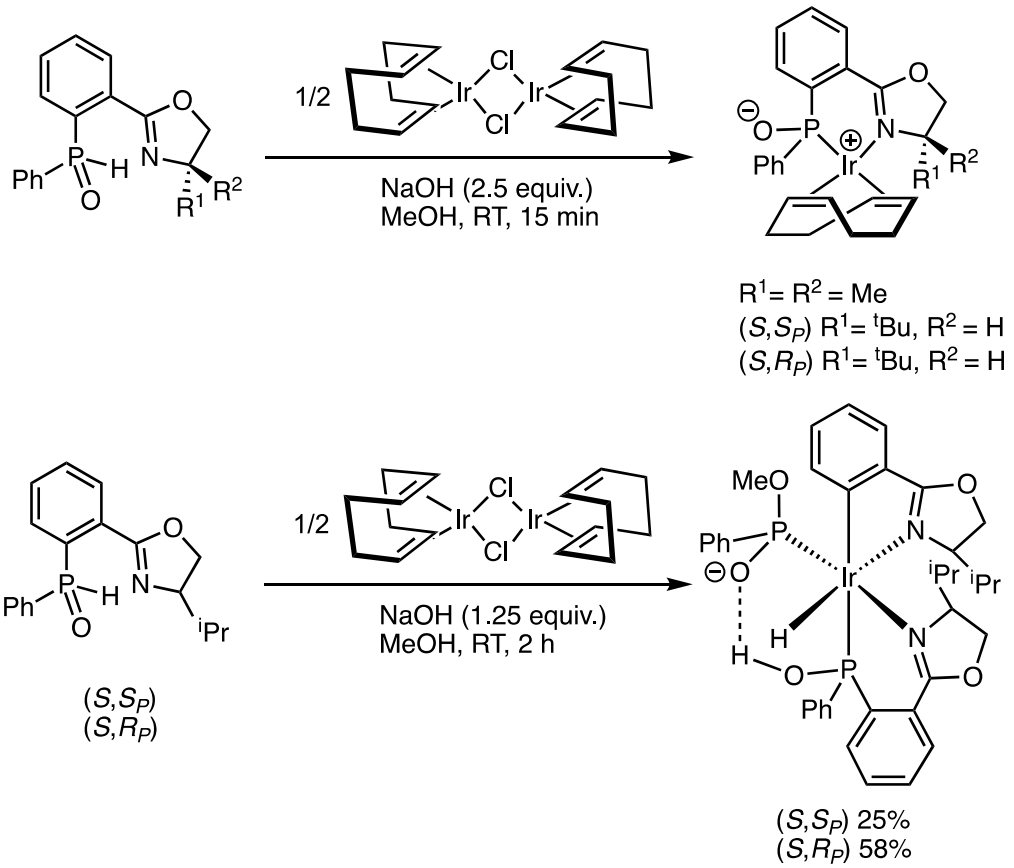


Scheme 45. Synthesis of the bis-coordinated Ir(I) complex.[133]

The complex was prepared reacting a solution of ligand ^{t}BuPh(O)H, with $[Ir(OMe)(COD)]_2$ dimer and two equivalents of water in THF at room temperature. Reaction with the analogous iridium precursor $[IrCl(COD)]_2$ containing the less-labile chloride anion affords the monomeric Ir(I) phosphinous acid complex. In contrast, the presence of water in the reaction media triggers the protonation of the methoxide and its subsequent release as methanol, which enables the introduction of the second SPO unit. Very recently the same group has described[134] that upon treatment of the complex with 5 bar of hydrogen a mixture of mono- and dihydride species was obtained, formed by oxidative addition of H_2 in a very diastereoselective process. The crystal structure of a dinuclear Ir(III) hydride could be obtained by X-ray diffraction.

There is little research carried out in the preparation of optically pure Ir-SPO complexes for its application in asymmetric catalysis. Pfaltz and co-workers[135] prepared a new SPO-oxazoline-type ligand containing a stereogenic centre located at the heterocyclic

ring, which was successfully coordinated to $[Ir(COD)Cl]_2$ under basic conditions. (Scheme 46)



Scheme 46. Preparation of optically pure Ir(I)-SPO-oxazoline complexes.

The corresponding zwitterionic Ir(I) complexes, containing a phosphinite, proved to be quite unstable for its use in asymmetric hydrogenation reactions. However, further exploration of its reactivity allowed the synthesis of an iridacycle containing an intramolecular hydrogen bridge. Treatment of neutral complex [Ir(COD)(PN-SPO)] or $[Ir(COD)Cl]_2$ under strong basic conditions in methanol, induces a P–Ar bond cleavage. The coordinated phosphorus unit is transformed into a phosphinic acid methyl ester by addition of methoxide, followed by the oxidation of Ir(I) to the Ir(III) hydride complex. Later release of COD and concomitant coordination of the SPO ligand leads to the formation of the iridacycle, a particular type of compounds that have displayed interesting results in asymmetric catalysis.[136,137]

A few years ago van Leeuwen, Cano and coworkers[82] presented a study describing the reproducible synthesis of iridium NPs stabilised by a few SPOs, starting from the dimer $[Ir(OMe)(COD)]_2$ as organometallic precursor under a hydrogen atmosphere. They were able to obtain small NPs that were full characterised by a wide range of techniques (including in-depth MAS-NMR studies), in order study the binding mode of

the ligands at the surface of the nanoparticles. They found evidence of three coordination modes: the SPO as a purely anionic ligand Ir–P(O)R_2, as a neutral Ir–P(OH)R_2 ligand and as a monoanionic bidentate H-bonded dimer R_2P–OH–H···O=PR_2, with the last mode being predominant for the more basic dicyclohexylphosphine oxide. The Ir/SPO NPs were used in the hydrogenation of cinnamaldehyde to the parent alcohol (Scheme 87).

4.5. Nickel

When considering catalyst design, the most used *d*-block metals have been noble metals such as iridium, rhodium, or palladium but at present there is a huge research effort on catalysis mediated by earth-abundant transition metals. The complexation of these metals to SPOs, however, has been rarely described.

For Ni(II), the first complex with a pseudobidentate bridge was described in 1977[138] with a few reports on related structures a few years later.[139,140]

In 2005, Han and co-workers[141,142] disclosed the nickel-catalysed hydrophosphinylation of terminal alkynes with a mixture of [Ni(PPh_2Me)$_4$] and Ph_2P(O)H.[141,142] They were able to generate *in situ* a five-coordinated hydrido phosphinito nickel complex, by means of an oxidative addition of diphenylphosphine oxide and [Ni(PEt_3)$_4$], which was characterised by ^{1}H NMR spectroscopy but not isolated (Figure 8).

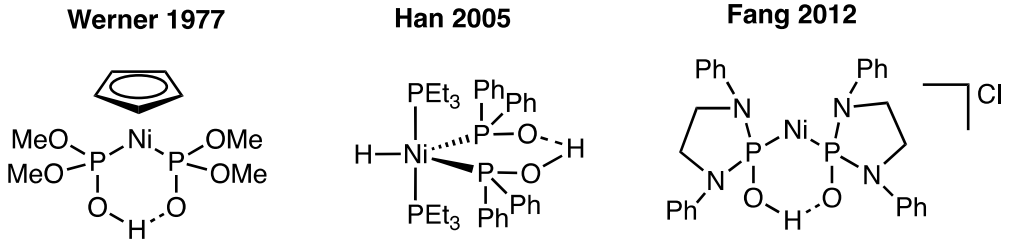
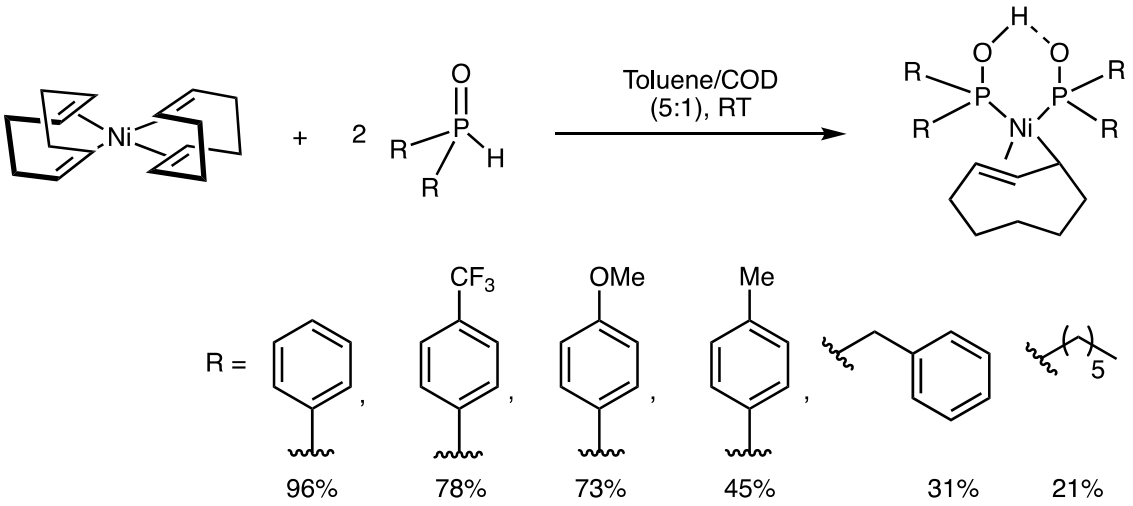


Figure 8. Reported Ni(II) complexes with SPOs.[141-144]

Some years later, Fang and co-workers[143,144] reported another catalytic application for "*in situ*" Ni-HASPO complexes, in this case, having diaminophosphine oxides as ligands which were reacted with Ni(II) sources for the coupling of deactivated aryl halides and tosylates with Grignard reagents (Kumada-Tamao-Corriu reaction).[143,144] These nickel complexes exhibited high activities in the Kumada-Tamao-Corriu coupling of electronically deactivated chlorides, fluorides and tosylates with Grignard reagents. Such a broad range of halides is rare in the literature. In addition, a small enantiomeric excess was found when a chiral HASPO was used.

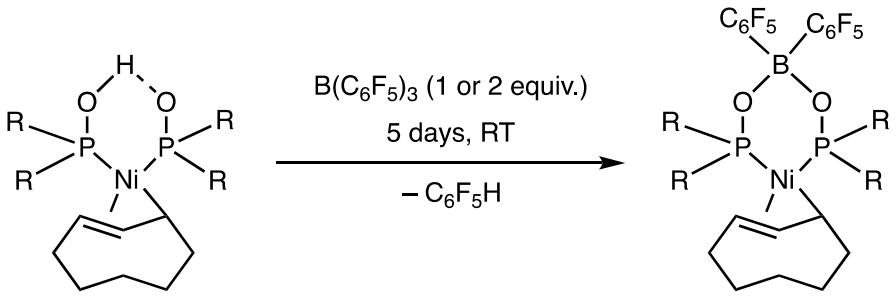
Cationic Ni(II) species are of interest for migratory insertion of olefins to produce polymers[139,145-147] but due to their high reactivity and their instability, are usually generated "*in situ*" from a nickel(II) halide precursor.[148]

More recently, Breuil and co-workers[149] reported that bis(cyclooctadiene)nickel(0), reacts with sulfonamido-phosphines in the presence of a second phosphine ligand, leading to a self-assembled supramolecular organometallic species. Further studies of the same research group disclosed the preparation of several diamagnetic π-allylic nickel complexes bearing a phosphinito-phosphinous acid system as stable solids (Scheme 47).[150]



Scheme 47. Ni-SPO allylic complexes prepared by Breuil and co-workers.[150]

This study[150] showed that when [Ni(COD)$_2$] reacts with the SPO ligand in toluene and an excess of COD, to prevent the formation of metallic nickel, the process yields the corresponding pseudobidentate π-allylic nickel(II) complexes. Lewis acid molecules such as boranes can easily substitute this labile intramolecular H-bridge, increasing the rigidity of the six-membered ring. In the case of the parent Ni systems, treatment of the pseudobidentate complexes with B(C_6F_5)$_3$ triggers the formation of the corresponding bidentate analogues (Scheme 48).

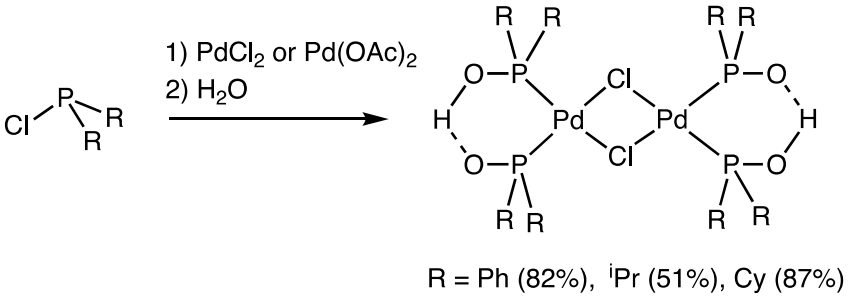


Scheme 48. Reactivity of SPO-nickel complexes.

In these studies it became evident again that basic and bulky aliphatic SPOs are much less reactive to [Ni(COD)$_2$]. Indeed, when they used the bulkier mesityl or iso-propyl SPO analogues only degradation to metallic nickel was observed.[150]

4.6. Palladium

Dixon and Rattray[151] were among the first[152,153] to convincingly describe dimeric palladium(II) complexes with two diphenylphosphine oxides acting as an anionic pseudobidentate ligand. The research on these Pd-SPO complexes received a boost in 2001 when Li and co-workers[30,31] used dialkylphosphinous acids in catalytic cross-coupling reactions.[154] In addition, the same type of compounds were successfully applied to the Suzuki-Miyaura couplings of aryl chlorides[155] and in Heck reactions of 4-chloroquinolines (Scheme 49).[156,157]



Scheme 49. Pd(II) SPO complexes reported by Li and co-workers.[31]

These complexes were prepared reacting a chlorophosphine with palladium chloride or acetate, followed by the addition of water and sometimes are obtained fortuitously by decomposition complexes with other ligands, highlighting their stability.[158,159] The dimeric nature of the complexes has been established by means of X-ray diffraction methods.[158-162]

The remarkable air-stability of these Pd systems made them attractive for its use as catalysts in C–C bond formation processes. This fact, together with the high activity of such Pd(II) SPO systems, particularly those containing electron-rich and sterically hindered alkyl substituents, spurred the research in the field. Wolf and co-workers[163] expanded these studies preparing a family of palladium complexes having, both monomeric and μ-chlorido-bridged dimeric structures (Figure 9) using the same synthetic procedures previously described by Li and co-workers.[31]

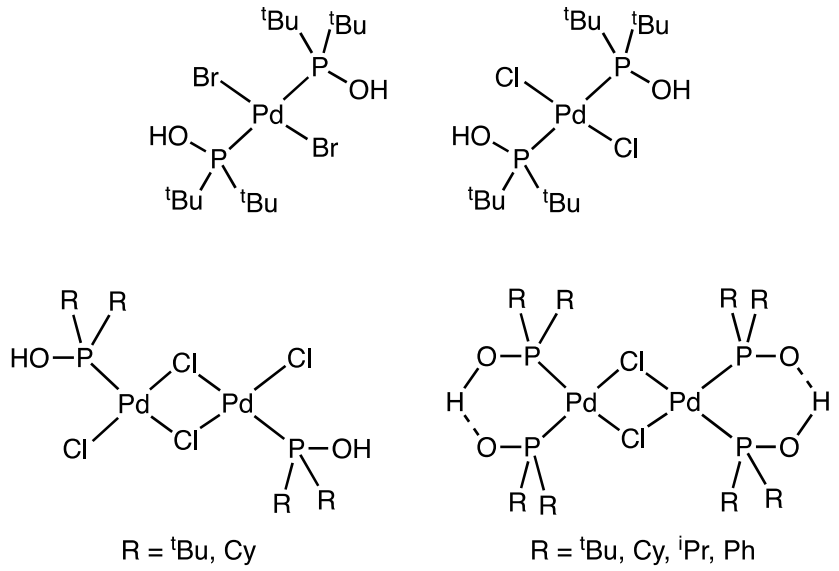
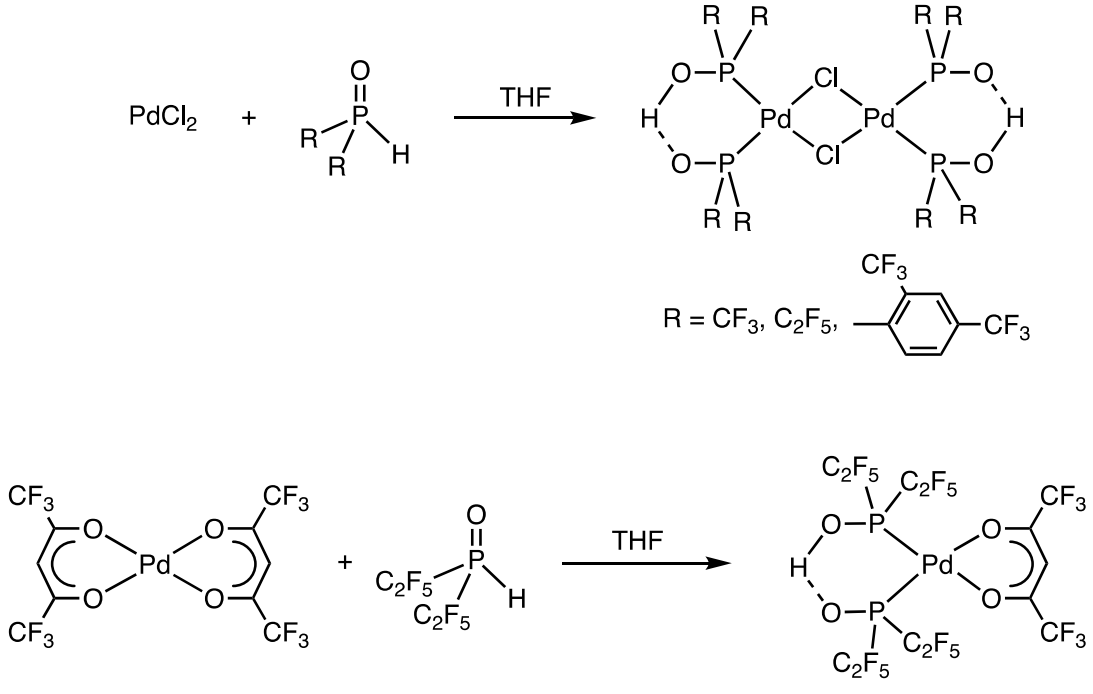


Figure 9. Pd(II) monomeric and dimeric SPO complexes described by Wolf and co-workers.[163]

Some dialkylchlorophosphine palladium complexes have also been isolated that easily give the corresponding SPO complexes by hydrolysis.[161]

The whole set of compounds was successfully applied in Suzuki-Miyaura cross-coupling reactions (Scheme 98) displaying good conversions with a wide range of electron-deficient and electron-rich aryl iodides, bromides and chlorides.[163]

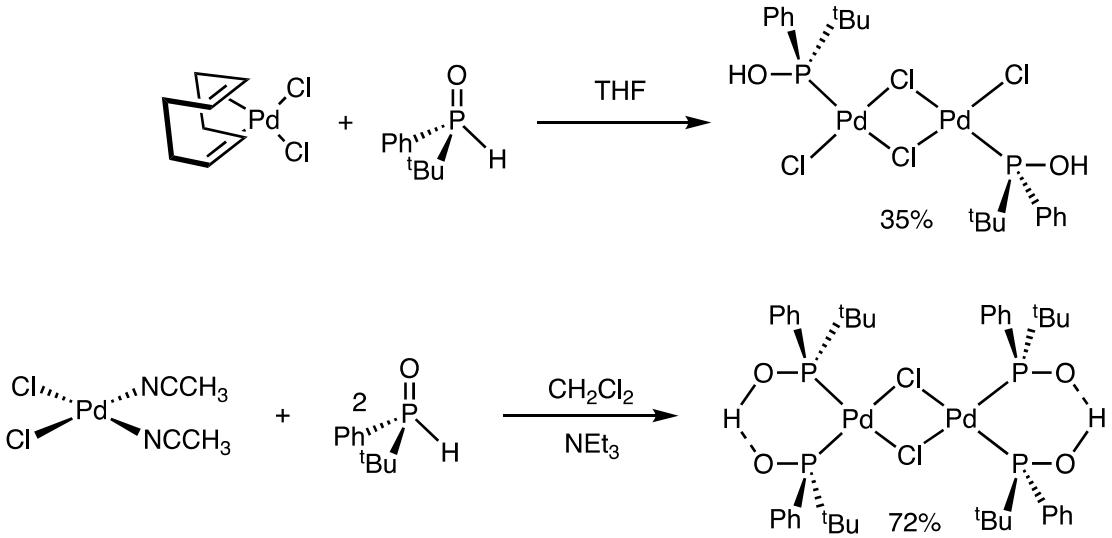
In order to study the influence of electron-deficient substituents on the catalytic activity of these processes, Hoge and co-workers[164,165] evaluated the coordination properties of bis-(trifluoromethyl)-, bis-(pentafluoroethyl)-, and bis[2,4-bis(trifluoromethyl)phenyl] phosphinous acids with Pd (Scheme 50).



Scheme 50. Electron-poor SPO-Pd(II) complexes prepared by Hoge and co-workers.[165]

Dimeric complexes were obtained reacting the ligands with palladium dichloride. In contrast, treatment of a solution $(C_2F_5)_2P(O)H$ (and other fluorinated SPOs)[164] with palladium bis(hexafluoroacetylactetonate) leads to the formation of a monomeric complex.[165]

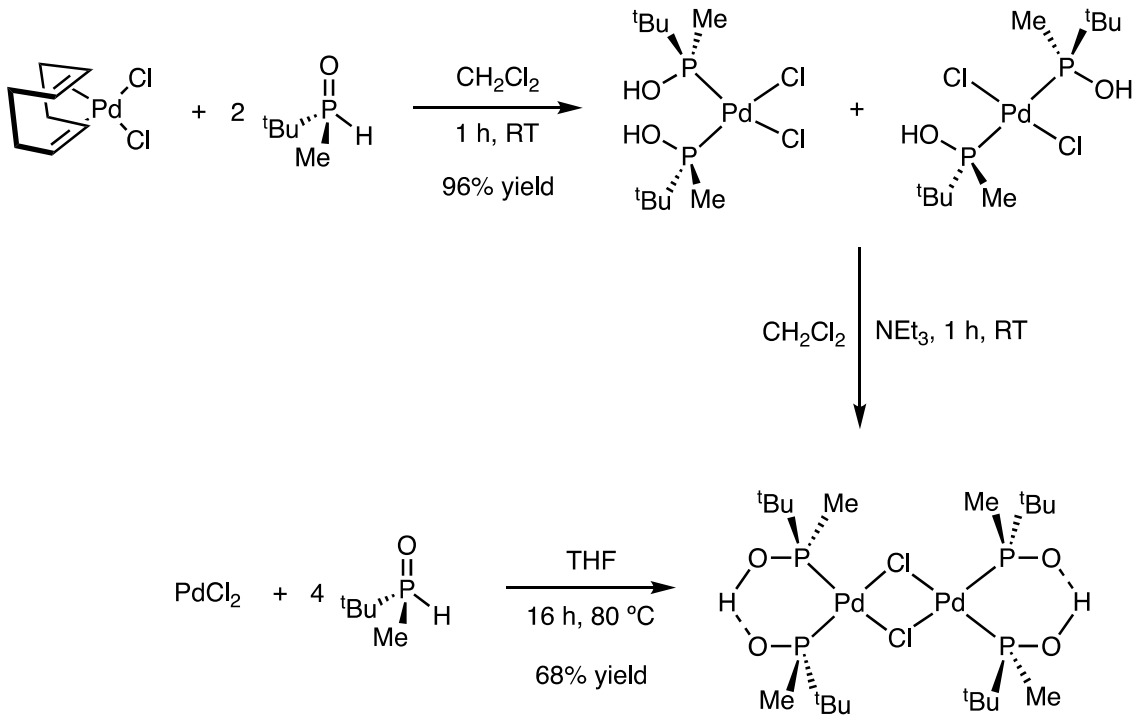
Despite the growing interest on the preparation of optically pure complexes for its application in asymmetric transformations, only a few examples of chiral Pd-SPOs can be found in the literature. The first attempts to obtain enantiomerically enriched palladium complexes were carried out in Dai laboratories using the optically pure (*S*)-^{t}BuPhP(O)H[86] (Scheme 51).



Scheme 51. Preparation of Pd(II) complexes with (*S*)-^{t}BuPhP(O)H.

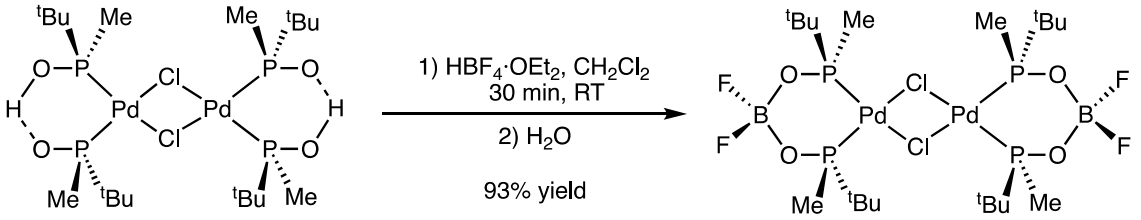
Reaction of $[PdCl_2(COD)]$ and two equivalents of SPO in THF affords the dinuclear monocoordinated complex, whereas the use of $[PdCl_2(CH_3CN)_2]$ in the presence of triethylamine as base leads to the pseudobidentate compound in moderate yields.

Having this literature precedents in mind, in our group we envisaged[69] the complexation of optically pure ^{t}BuMeP(O)H to Pd precursors, following the methods developed by Li and co-workers[30] and by Buono and co-workers[166] for related Pt compounds. Therefore, when (*S*)-^{t}BuMeP(O)H was treated with $[PdCl_2(COD)]$ a mixture of *cis* and *trans* isomers was observed (Scheme 52).



Scheme 52. Preparation of Pd complexes with the optically pure (*S*)-^{t}BuMeP(O)H.

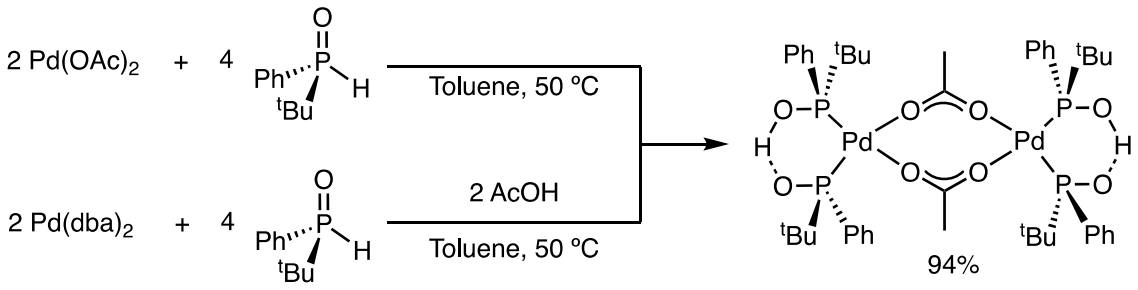
Addition of NEt_3 formed smoothly the desired dimeric phosphinito-phosphinous acid palladium complex with excellent yields.[69] This complex appeared to be very stable since after some experimentation it was found that it could be prepared by simply refluxing $PdCl_2$ in THF in air, in the absence of base. Furthermore, the pseudobidentate bridge could be straightforwardly transformed into a *real* bidentate unit upon treatment with tetrafluoroboric acid (Scheme 53).[69]



Scheme 53. Substitution of the OH bridge by BF_2 in the dinuclear optically pure Pd complex.

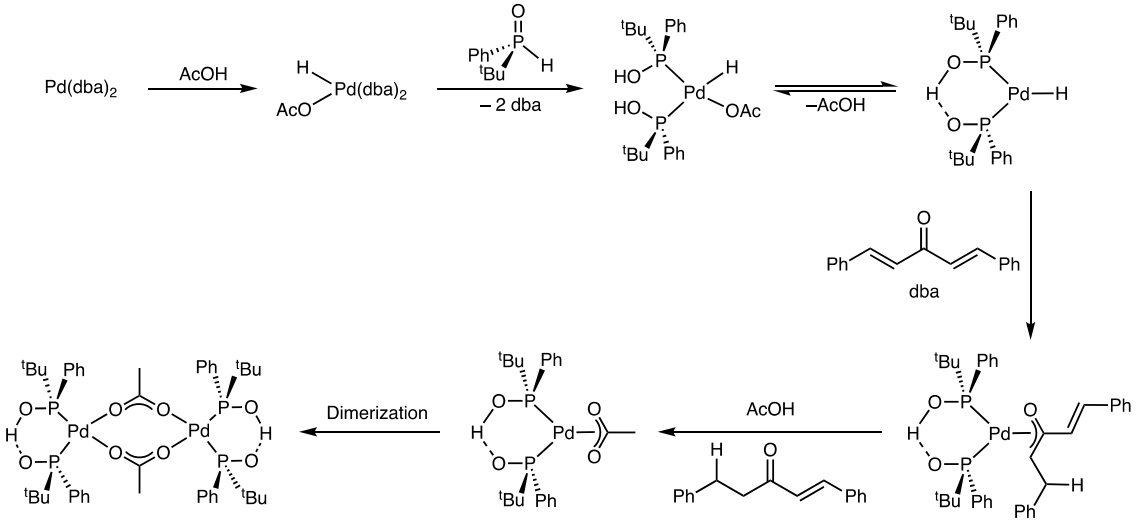
The lability of the bridging ligand in Pd(II) SPO dinuclear complexes, appears to have an important influence in the catalytic processes. Indeed, Buono, Giordano and co-workers[166-168] described an unprecedented application for dimeric acetate-Pd complexes, having the ^{t}Bu/Cy combination in the SPO ligands, in the [2+1] cycloaddition reaction/ring expansion of alkynes with norbornadiene derivatives (Scheme 104). An account by Clavier and Buono on the Pd- and Pt-phosphinous acids and their applications in this type of reactions has recently appeared.[169]

Some described complexes contain a bridging-acetato ligand between the two Pd(II) centres and the optically pure ^{t}BuPhP(O)H moiety (Scheme 54).



Scheme 54. μ-acetato dimeric Pd complexes reported by Buono, Giordano and co-workers.[166-168]

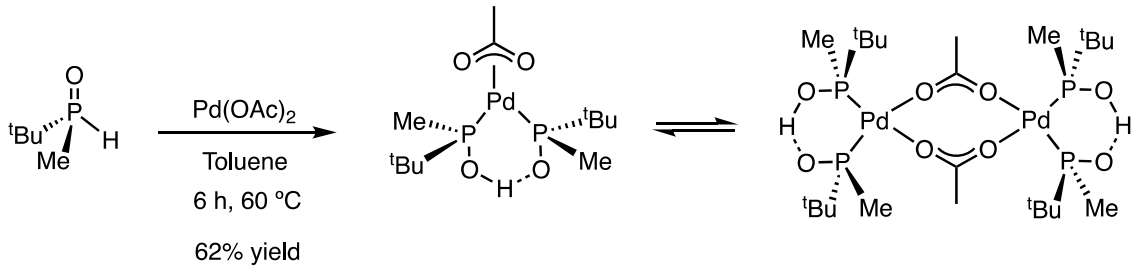
The formation of the palladium dimer is thought to occur by means of a ligand exchange of dba by SPO after oxidative addition of acetic acid to Pd(0) to give the Pd-hydrido monomer (Scheme 55).



Scheme 55. Proposed reaction pathway for the formation of the Pd dinuclear complex.

The loss of AcOH, coordination of dba and later insertion of the olefin moiety into the palladium-hydride bond affords a Pd(II) enolate intermediate that quickly evolves into the monomeric acetate complex. Subsequent dimerization furnishes the desired μ-acetato bridged system.

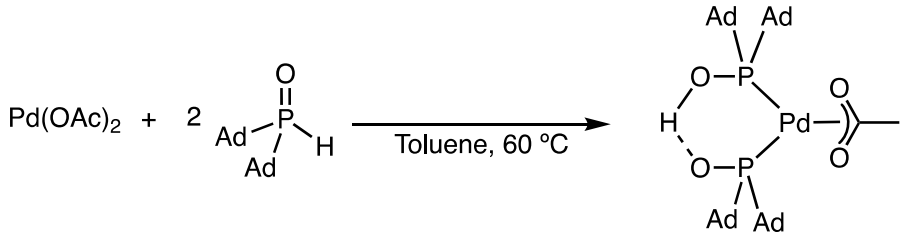
These Pd SPO complexes were also studied in our group[69] reacting palladium(II) acetate with optically pure (*S*)-^{t}BuMeP(O)H (Scheme 56).



Scheme 56. Preparation of Pd acetate complexes with (*S*)-^{t}BuMeP(O)H.

Interestingly, when the ligand was treated with $Pd(OAc)_2$ in refluxing toluene according to previous methodologies.[35,166,167,170] a mixture of monomeric and dimeric species in a 1:1 ratio was found.

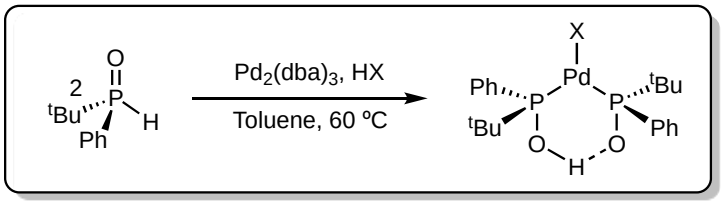
The increase of the bulkiness of the SPO favours the formation of the monomeric species as it has been described by Ackermann and co-workers (Scheme 57).[170]

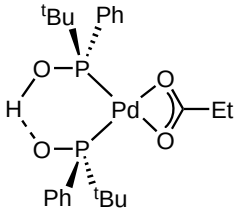


Scheme 57. Preparation of the Pd(II) acetate complex with $(Ad)_2P(O)H$.

Hence, reaction of palladium(II) acetate with two equivalents of $Ad_2P(O)H$ in toluene exclusively forms the pseudobidentate monomeric acetato-complex, which has displayed high catalytic activity in the cross-coupling of 2-pyridyl Grignard reagents.[170]

The promising catalytic activity of these palladium complexes have set these systems in the spotlight, and very recently, Nuel, Giordano and Martínez[171] have successfully prepared a family of *P*-stereogenic biphosphinite palladacycles through a H-transfer-based self assembly process (Scheme 58).





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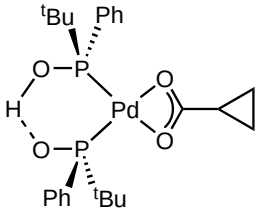

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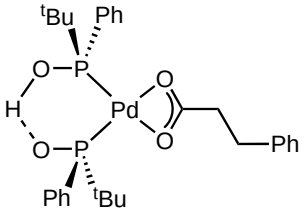

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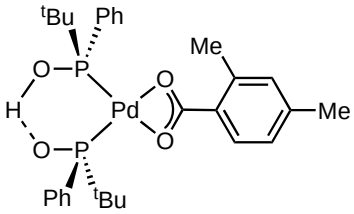

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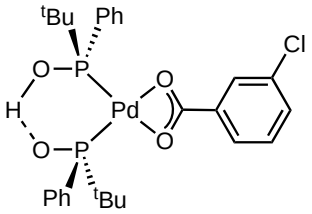

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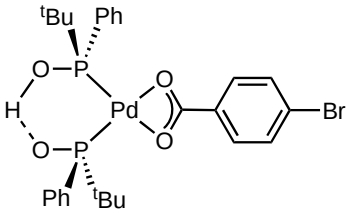

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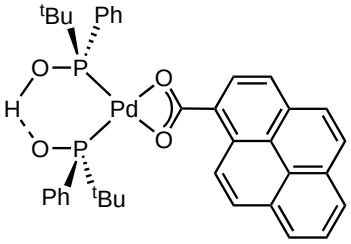

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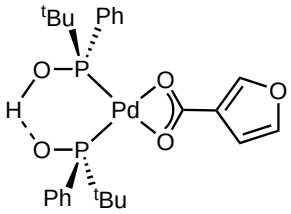

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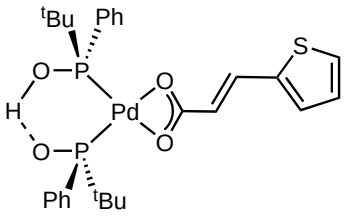

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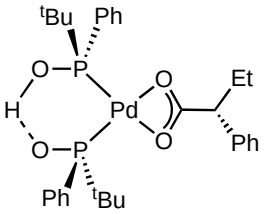

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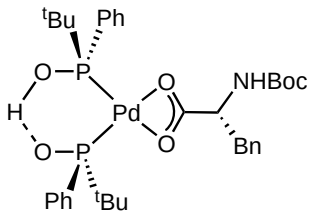

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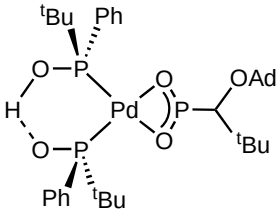

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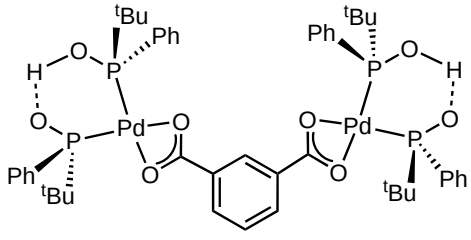

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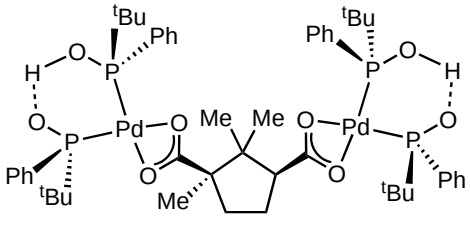

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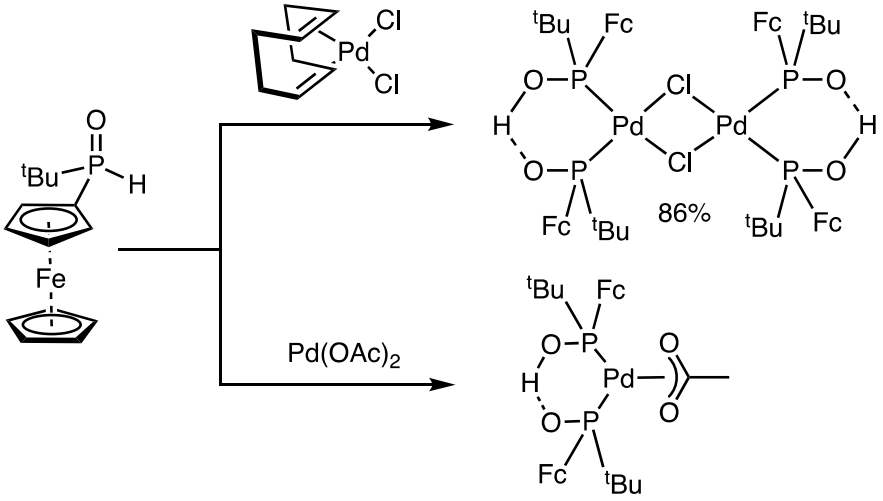
Scheme 58. Chiral bisphosphinite palladacycles described by Nuel, Giordano and Martínez.[171]

The reaction is thought to occur through the oxidative addition of an acid HX to Pd(0) followed by the *cis* coordination of two SPO units.

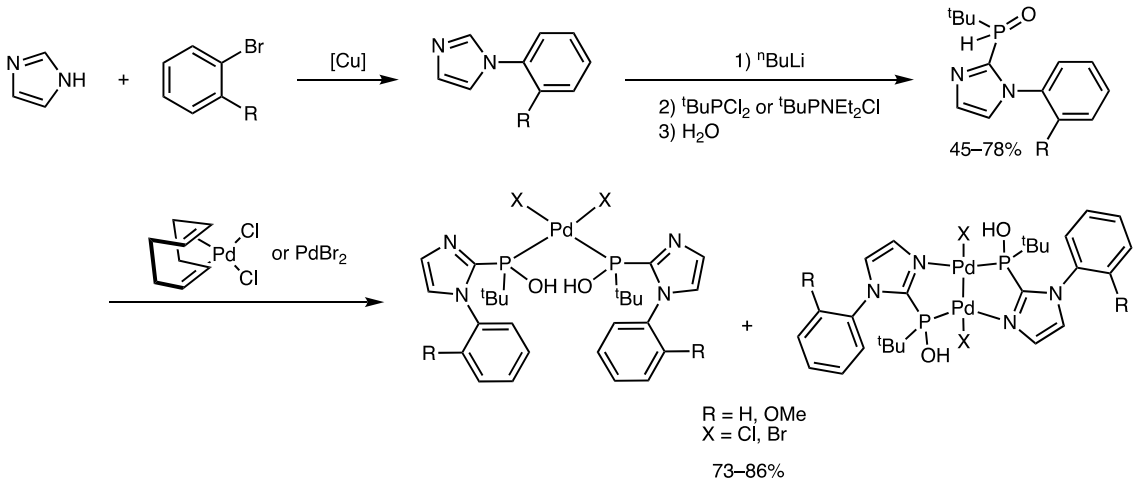
Hong and co-workers[35] described the preparation of ferrocenyl-derived SPOs (Scheme 8) and their application in Suzuki-Miyaura cross-coupling reactions (Scheme 59).



Scheme 59. Preparation of Pd/SPO complexes bearing a ferrocenyl substituent.

Ferrocenyl SPOs can be synthesised by lithiation of ferrocene and reaction with the corresponding aminochlorophosphine derivative, which after treatment with SiO_2/CTLC yields the desired SPO. Alternatively, the ligand can be also obtained by hydrolysis of the ferrocenyl-derived chlorophosphine. Coordination of the ligand with the due palladium source afforded the dinuclear μ-chlorido bridged complex and the monomeric acetato species, respectively.[35] Interestingly, the pseudobidentate architecture can be achieved, also, introducing another SPO in the ferrocenyl unit (Scheme 59).[35]

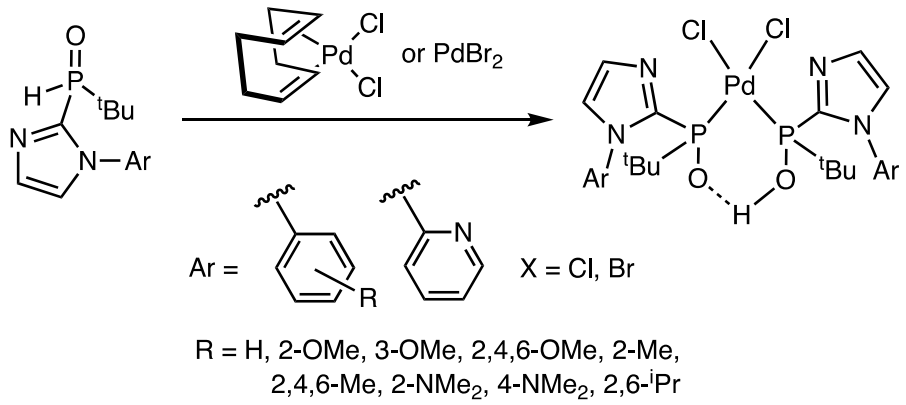
With the aim of improving the efficiency of several C–C catalytic bond formation reactions, other Pd-SPO systems have been explored. Particularly interesting are those containing heterocyclic-based secondary phosphine oxides, which has promoted excellent results in Heck reactions, as it has been described by Hong, Shaikh and co-workers (Scheme 60).[6,172]



Scheme 60. Preparation of imidazole-based SPO-Pd complexes.

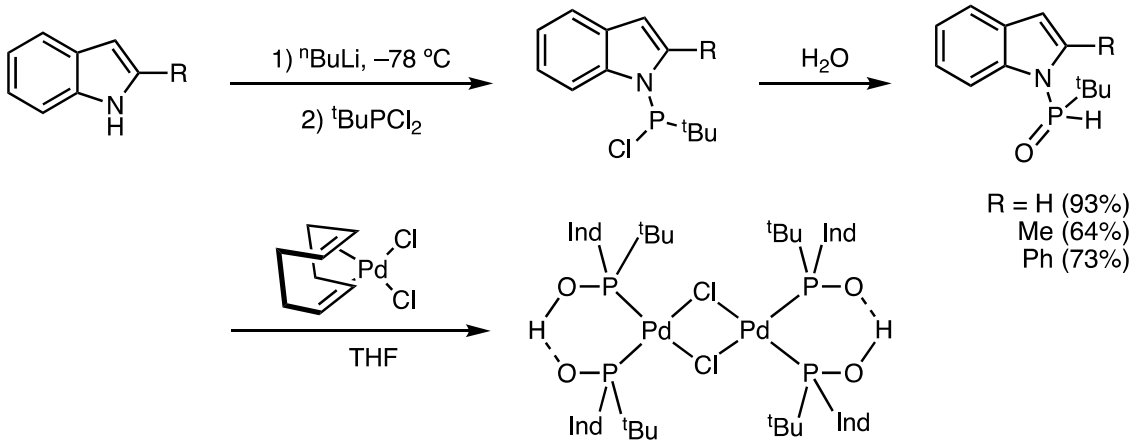
Cu-promoted coupling of imidazole and 2-bromoarenes followed by sequential deprotonation, addition and hydrolysis of a chlorophosphine derivative, yielded the imidazole-derived SPOs. Later coordination with [$PdCl_2$(COD)] triggered the formation of the expected *cis* Pd(II) complex, albeit without the pseudobidentate coordination. A rare Pd(I) dinuclear cluster containing a Pd–Pd bond was also formed in the reaction course, both using palladium(II) bromide or [$PdCl_2$(COD)] as starting reagents.

The pseudobidentate chelation has been recently achieved by Hong's group introducing a ^{t}Bu substituent at the phosphorus atom (Scheme 61).[173]



Scheme 61. Preparation of pseudobidentate imidazole-derived Pd complexes.

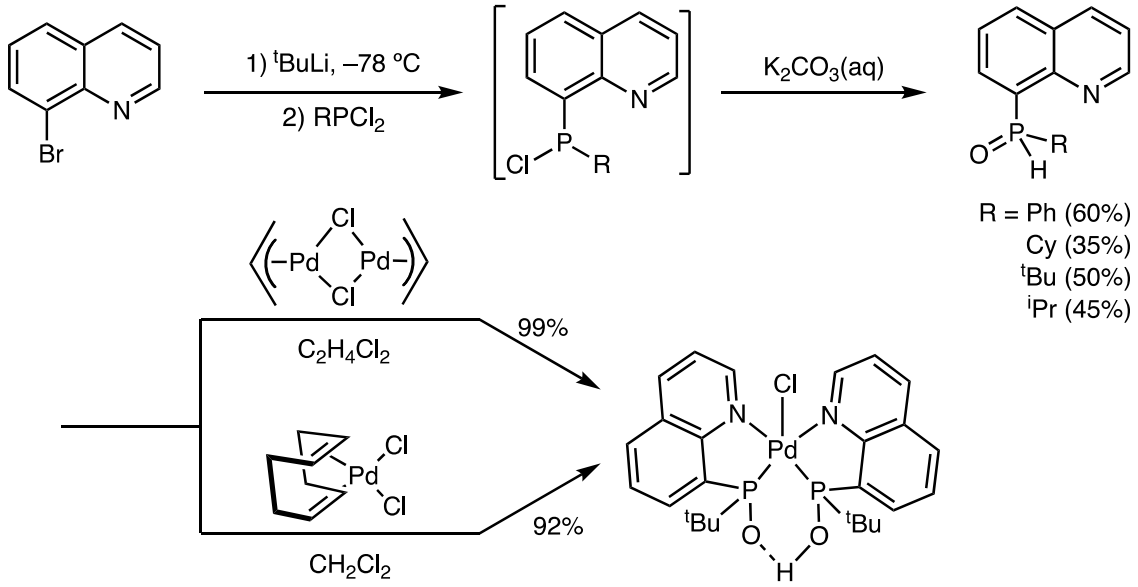
Hong and his co-worker[174] also reported the preparation of indolyl-substituted secondary phosphine oxides in which the N of the heterocycle acts as an hemilabile centre (Scheme 62).



Scheme 62. Synthesis of indolyl-SPOs and formation of the dimeric Pd complex.

In this case, coordination of the heterocyclic-based SPO to [$PdCl_2$(COD)] yielded the μ-chlorido-bridged palladium dimer, rather than the monomer.

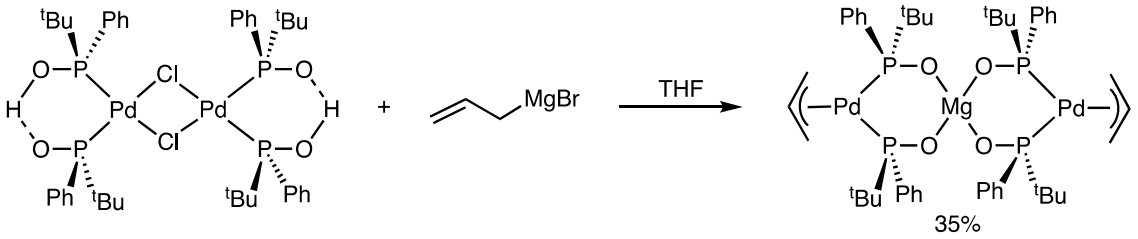
Introduction of the bulky quinolyl group in the SPO triggered the formation of the mononuclear complexes (Scheme 63), reported by the same group.[175]



Scheme 63. Mononuclear pentacoordinated Pd complex with a heterocyclic SPO.

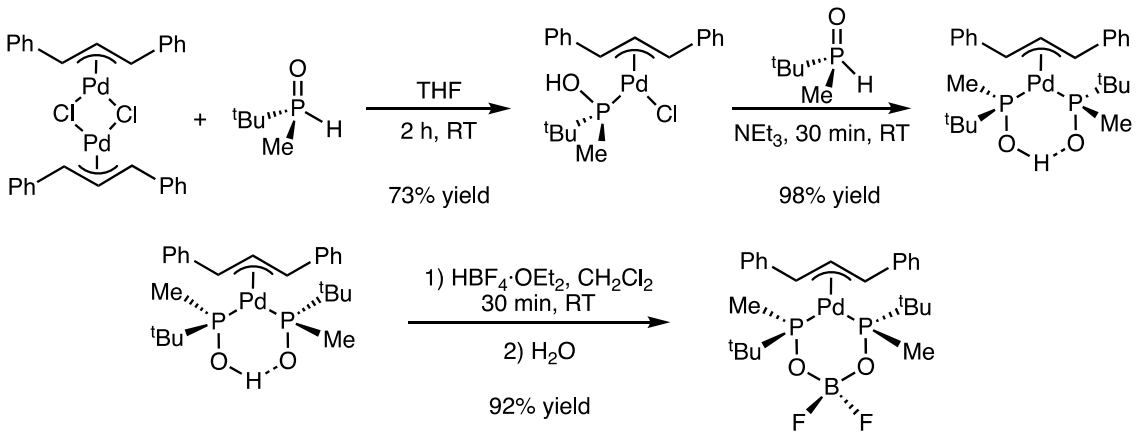
The reaction of allylpalladium dimer or [$PdCl_2$(COD)] did not furnish the expected allyl-Pd and dichloro-Pd species respectively, but the same pentacoordinated Pd complex instead. This complex displayed an uncommon (for Pd(II) complexes) distorted square-pyramidal geometry, having an apical chlorido ligand, and two bidentate SPO ligands with an intramolecular hydrogen bridge.

The preparation of allyl-palladium complexes with SPOs has been scarcely explored. Only Dai and co-workers[86] described in 2003 a dimeric optically pure complex containing two allyl frameworks linked by a magnesium centre (Scheme 64).



Scheme 64. Preparation of the optically pure allyl Pd complex reported by Dai and co-workers.[86]

In the view of these results in our group studied the reactivity of different allyl Pd precursors with the enantiomerically enriched ^{t}BuMeP(O)H. Only the 1,3-diphenylallyl group allowed the isolation of the optically pure Pd-SPO complex (Scheme 65).[69]

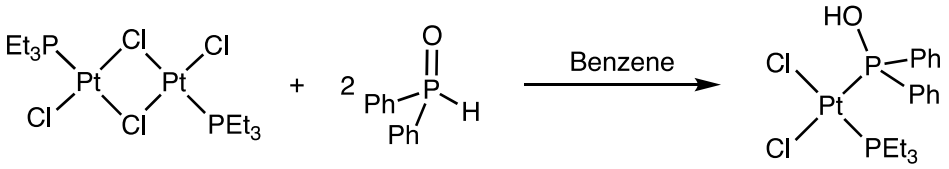


Scheme 65. Preparation of optically pure allylPd complexes with ^{t}BuMeP(O)H and substitution of the OH bridge by BF_2.

Later treatment with $HBF_4{\cdot}OEt_2$ was carried out in order to form a BF_2 bridge, leading to the corresponding complex with bidentate ligand, which was crystallographically characterised.

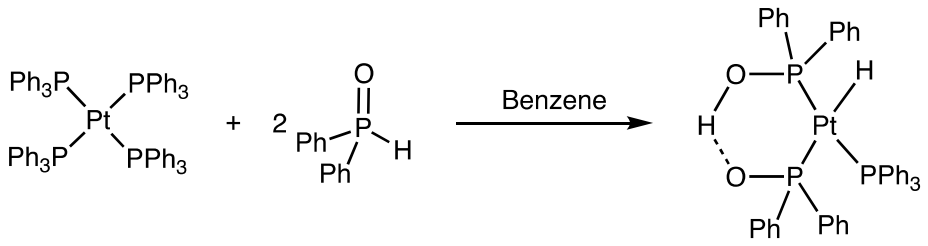
4.7. Platinum

The coordination chemistry of Pt with SPOs has been comparatively less explored compared to Pd. The first study was carried out by Chatt and coworkers[4] with the synthesis of Pt(II) complex *cis*-$[PtCl_2(PPh_2OH)(PEt_3)]$ by the reaction of the dimeric precursor $[PtCl(\mu\text{-}Cl)(PEt_3)]_2$ with diphenylphosphine oxide (Scheme 66).



Scheme 66. Synthesis of Pt(II) complex *cis*-[$PtCl_2(PPh_2OH)(PEt_3)$] reported by Chatt and co-workers.[4]

A few years later Roundhill and co-workers[176] studied the reaction of [$Pt(PPh_3)_4$], again with diphenylphosphine oxide in benzene. Interestingly they found that the reaction occurred with an oxidation of Pt(0) to Pt(II) followed by the formation of a phosphinito-phosphinous acid bridge (Scheme 67).



Scheme 67. Synthesis of Pt(II) complex bearing a pseudobidentate bridge reported by Roundhill and co-workers.[176]

These complexes, along a rather unnoticed report of Dixon and Rattray[151] on Pd and Pt complexes with diphenylphosphinito-diphenylphosphinous acid sit among the first examples of coordination compounds that bear the combination of a coordinated phosphinous acid and a phosphinito ligand, self-assembled through intramolecular hydrogen bonding.[7,32] It is interesting to note that the crystal structure of the complex with diphenylphosphinous acid was not reported until much later.[177] Although they were not specifically designed for this purpose, these early examples showed that anionic electron-rich phosphorus species could be prepared using air-stable SPOs.

Inspired by these works, van Leeuween and co-workers[5] described the first application of this Pt(II) pseudobidentate complex as a catalyst for the Pt-catalysed hydroformylation of olefins, renewing the interest on the field.[5]

In 1995 Ghaffar, Parkins and co-workers[178] studied Pt(II) complexes containing $HP(O)Me_2$ units (Figure 10) as catalysts for the hydrolysis of nitriles to amides and some of them in the hydration of the more challenging cyanohydrins.[179]

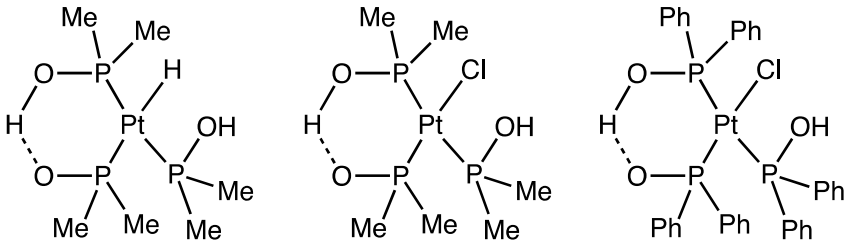
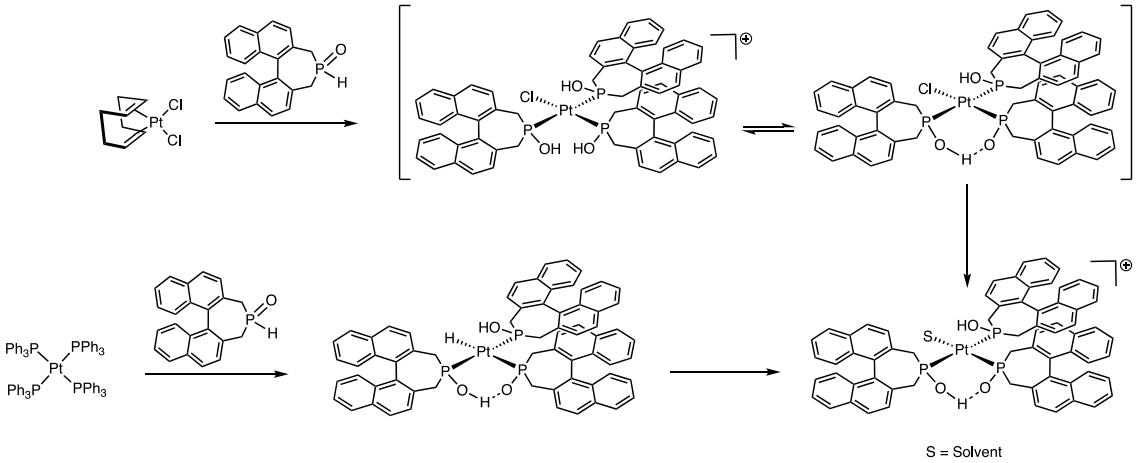


Figure 10. Pt(II) complexes as catalysts for the selective hydrolysis of nitriles to amides.

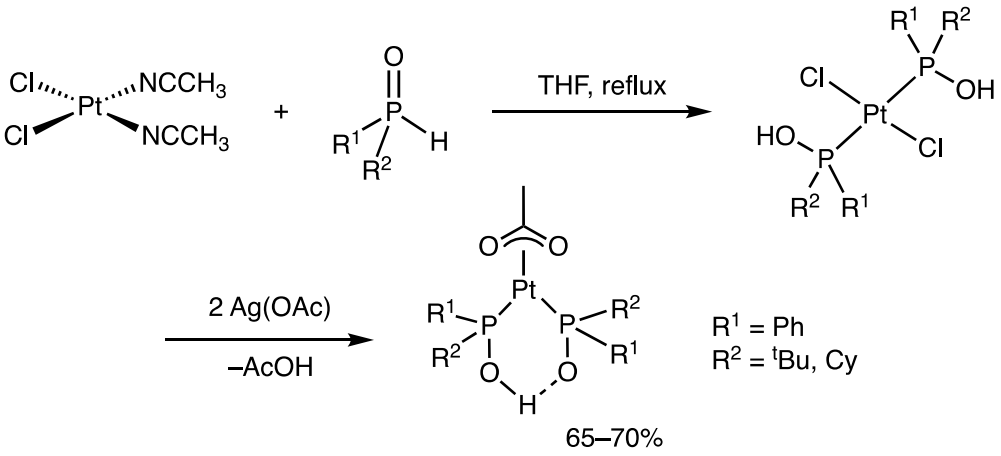
More recently these studies have been further explored by van Leeuwen and co-workers[180] in the use of "*in situ*" Pt(II) systems modified with chiral non-racemising SPOs, which has been successfully applied in nitrile hydration reactions. They gave some mechanistic insights on the species involved in the catalytic process (Scheme 68).



Scheme 68. Substitution on Pt(II) SPO complexes.

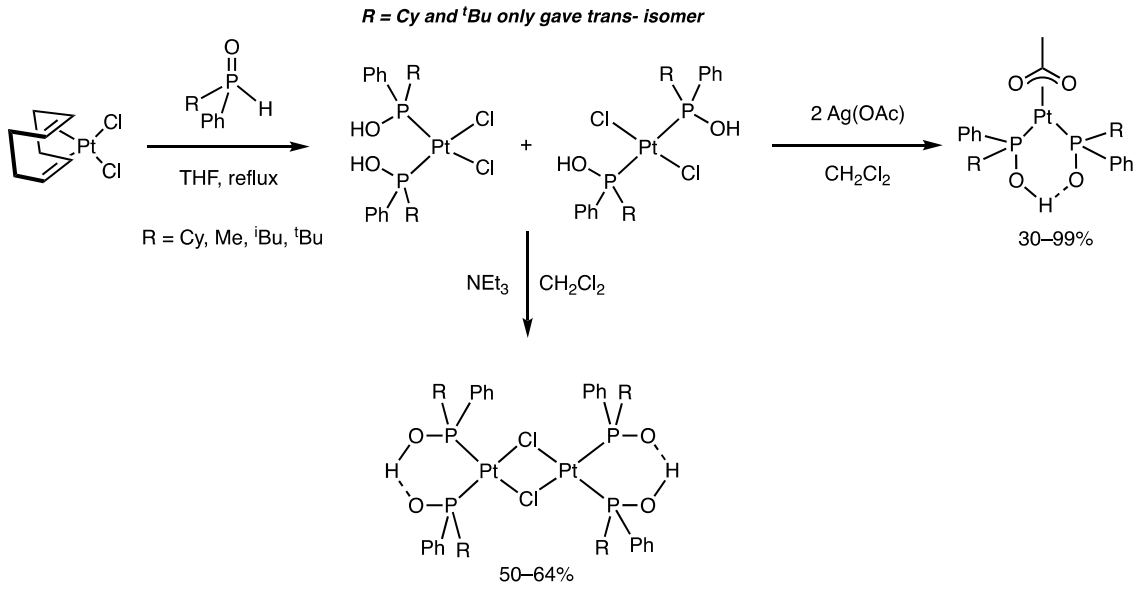
Hence, in the presence of [$PtCl_2$(COD)] and excess of the ligand, coordination of two units and formation of the intramolecular H-bridge was expected.[180] The *trans*-labilising effect of the P moieties allows the coordination of another SPO. Final release of the remaining ancillary Cl forms the catalytically active species, which can be alternatively achieved upon treatment of [$Pt(PPh_3)_4$] with an excess of the SPO.

Surprisingly, it was not until 2007 when a renewed interest emerged in the preparation of stable Pt-SPO complexes that could be used as preformed catalysts. Inspired by the pioneering work of Li and co-workers in 2001 in the application of Pd-SPO coordination compounds in various catalytic transformations,[156] Buono and co-workers[181] described the preparation of novel [Pt(η^2-acetato){RPhPO}$_2$H] complexes (Scheme 69) and their application to the benzylidenecyclopropanation of norbornadienes.



Scheme 69. Preparation of Pt-acetato SPO complexes described by Buono and co-workers.[181]

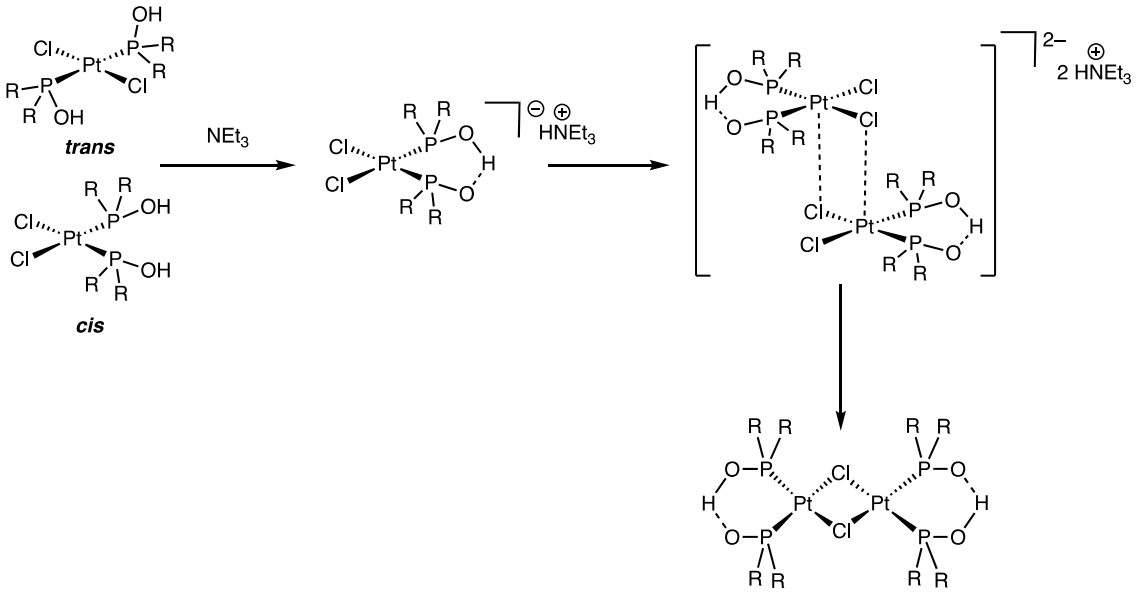
Preparation of these complexes was carried out reacting two equivalents of the corresponding SPO with $[PtCl_2(CH_3CN)_2]$ furnishing the dicoordinated *trans*-Pt isomer as a major product (Scheme 69), as also observed by other authors with bulky SPOs.[164] Noteworthy to mention is that reaction of optically pure (*R*)-*tert*-butylphenylphosphine oxide after 12 h in refluxing THF yielded a mixture of *cis*- and *trans*- complexes, in which partial racemisation was observed.[181] The authors proved that the equilibrium between the *cis*- and *trans*- did not induce racemisation, running the same reaction at room temperature using $[PtCl_2(COD)]$ as starting material, where a 1:1 mixture of isomers was formed but without optical erosion. Later exchange of chlorido ligand by acetate took place by addition of AgOAc, resulting in the formation of the corresponding *cis*-neutral complex, and the release of acetic acid[182] (Scheme 70).



Scheme 70. Coordination behaviour of Platinum SPO complexes reported by Buono and co-workers.[182]

Treatment of the *cis*-, *trans*- mixture with triethylamine triggered the formation of the dinuclear pseudobidentate palladium complex, which displays the two palladium centres in a square planar geometry according to X-ray diffraction studies.

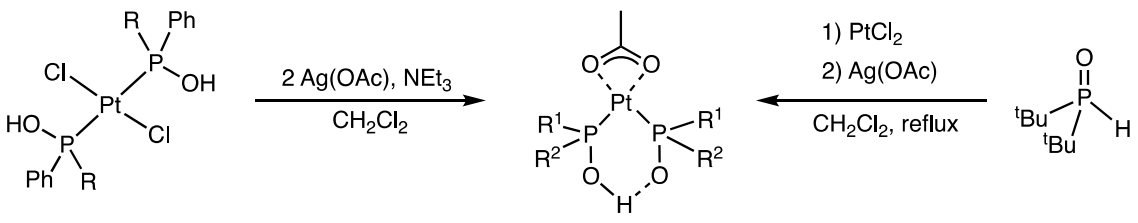
Furthermore, Giordano, Buono and co-workers[182] proposed a mechanism for the dimer formation that is depicted in Scheme 71 for a general case.



Scheme 71. Mechanism of dimerisation of Pt-SPO complexes.

The formation of the dinuclear complex might be explained by association of two pseudobidentate Pt(II) units, generating a 18 electron intermediate. The first step of the mechanism depends on the stereochemistry of the biscoordinated Pt(II) complexes. Hence, only those containing a *cis*- geometry are able to form the pseudochelated building block for the assembly process. The *trans*- analogues (which are formed in the presence of bulky substituents attached to P) appeared to be unreactive towards triethylamine, suggesting a pre-equilibrium between the *cis* and *trans*- complexes, which is shifted upon formation of the chloride-bridged product.

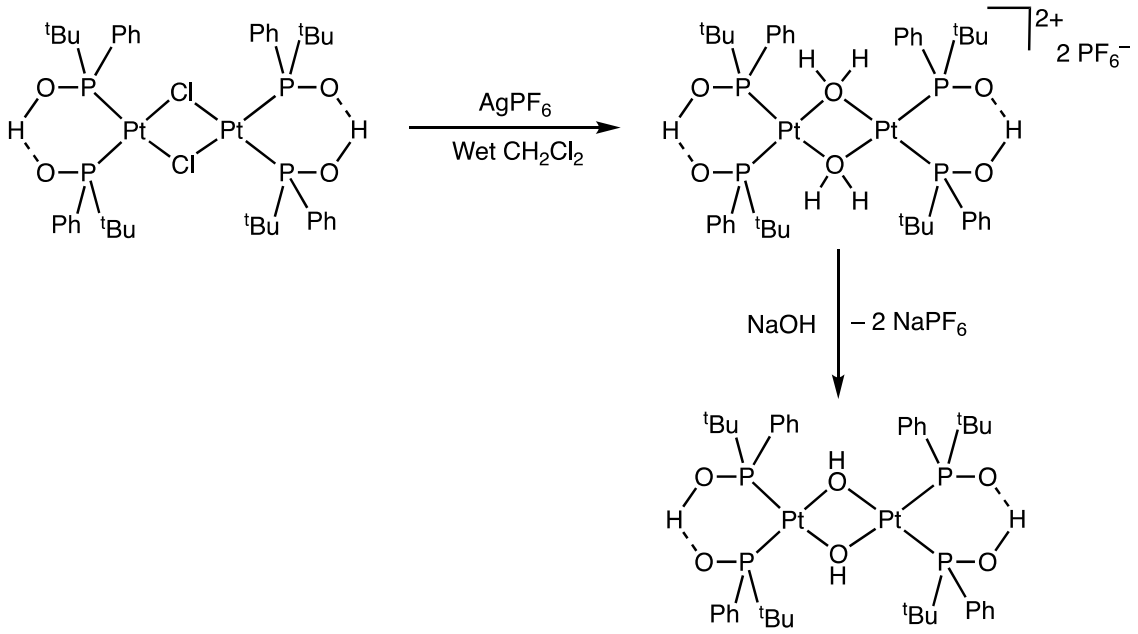
As it has been mentioned, sterically hindered groups on the P atom, such as ^{t}Bu, lead to the corresponding *trans*-Pt(II) complexes. Despite that they are unreactive towards NEt_3 they do react in the presence of AgOAc and a base to furnish the Pt(κ^2-acetato) SPO complexes[182] (Scheme 72).



Scheme 72. Formation of κ^2-acetato Pt SPO complexes.

This unusual κ^2-acetato complex can be also prepared by refluxing $PtCl_2$ with silver acetate as reported by Giordano, Buono and co-workers.[182]

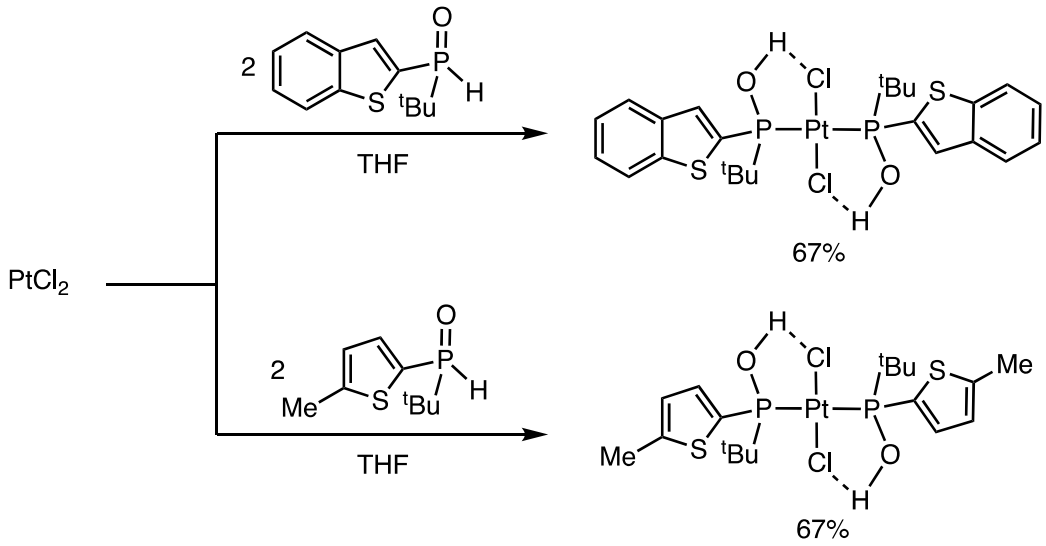
The reactivity of the Pt(II) dinuclear complexes have been explored recently by Martínez, Giordano, Nuel and co-workers[183] in their studies on the aerobic/anaerobic oxidation of several alcohols (Scheme 73).



Scheme 73. Reactivity of dinuclear Pt-SPO systems.

Abstraction of the bridging chlorido ligands with silver hexafluorophosphate in wet dichloromethane forms the dicationic complex with two coordinated water molecules, which can be easily deprotonated in basic media to furnish the neutral hydroxo-bridged platinum complexes.

In the search of more efficient catalysts for Suzuki-Miyaura cross-couplings and Catellani reactions, Hong and co-workers[184] described the preparation of heterocyclic substituted SPOs and their coordination to Pt systems (Scheme 74).

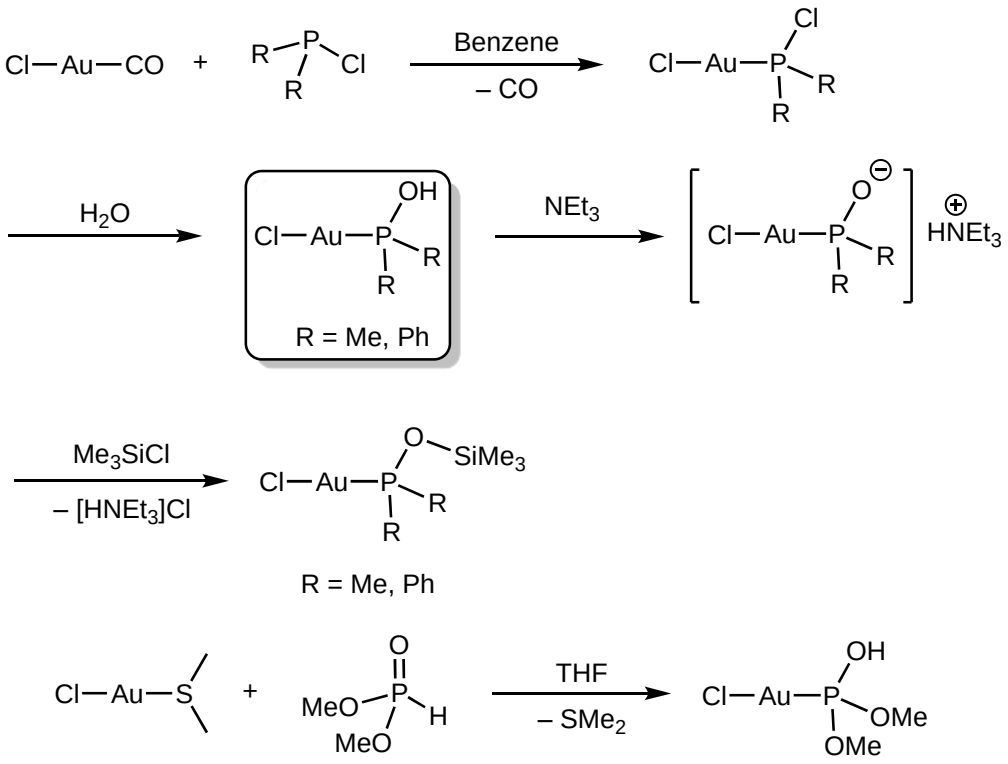


Scheme 74. Preparation of SPO-heterocyclic Pt complexes.

Reaction of SPO with a heterocyclic substituent with $PtCl_2$ in THF showed the expected formation of the *trans*- Pt complexes, which displays interactions between the terminal OH moiety and the Cl ligands in the solid state.

4.8. Gold

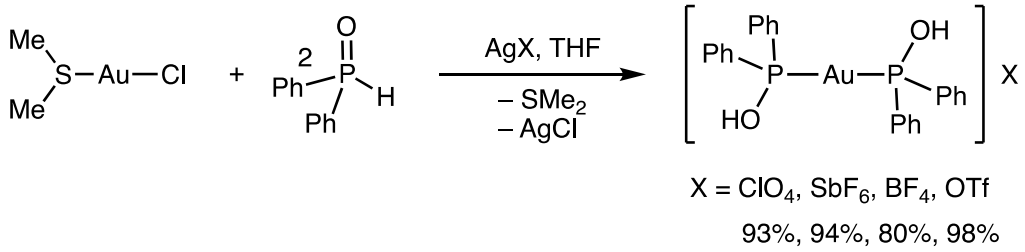
The coordination chemistry of gold(I) with SPO ligands has been little explored. The first examples were reported by Schmidbaur and co-workers[185-188] with phosphinous acid ligands (Scheme 75).



Scheme 75. Synthesis of Au(I)-SPO complexes.[185]

Reaction of [ClAu(CO)] with a chlorophosphine affords a complex with loss of CO that was not isolated but formed the corresponding Au(I) phosphinous acid complex by hydrolysis. Further reaction with Me_3SiCl leads to the silylated complex. The same reaction has been carried out using SMe_2 as leaving group in the Au(I) precursor and dimethyl phosphonate. Its corresponding gold-phosphinite complex could be obtained upon deprotonation with triethylamine.

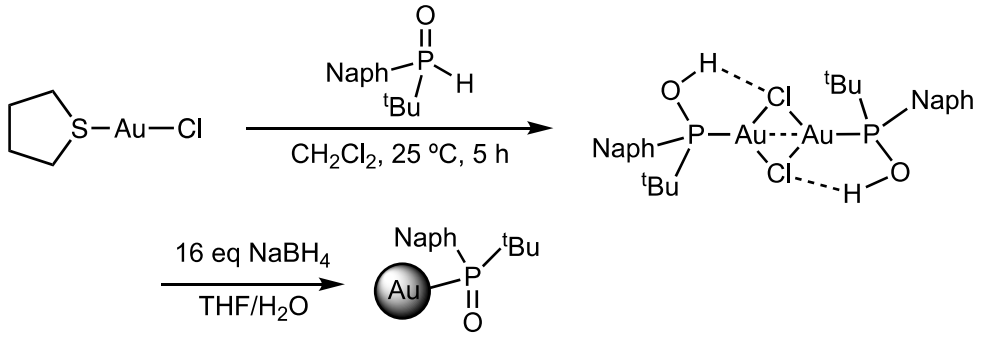
Substitution of two phosphine units have been also achieved by Schmidbaur and co-workers[185-187] (Scheme 76).



Scheme 76. Preparation of disubstituted Au(I)-SPO complexes.

Disubstituted gold(I) phosphinous acid complexes were obtained by reaction of $[(Me_2S)AuCl]$ with two equivalents of $Ph_2P(O)H$ in the presence of silver salts of non-coordinating anions.[185-187]

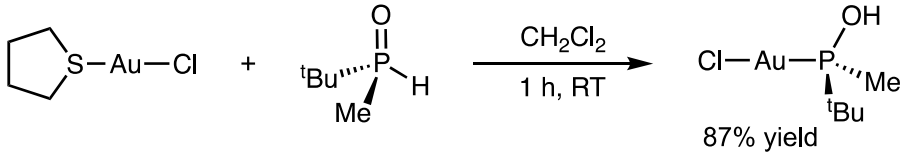
More recently, van Leeuwen and co-workers[189,190] used the complex [^{t}Bu(1-naphthyl)P(OH)AuCl]$_2$ as a precursor for gold nanoparticles that proved to be active for the hydrogenation of substituted aldehydes (Scheme 77).



Scheme 77. Preparation of gold(I) nanoparticles described by van Leeuwen and co-workers.[189,190]

At the same time Schröder and co-workers[191] described the first use of molecular systems in enyne cycloisomerisation and hydroxy- and methoxycyclisation reactions (Scheme 80).

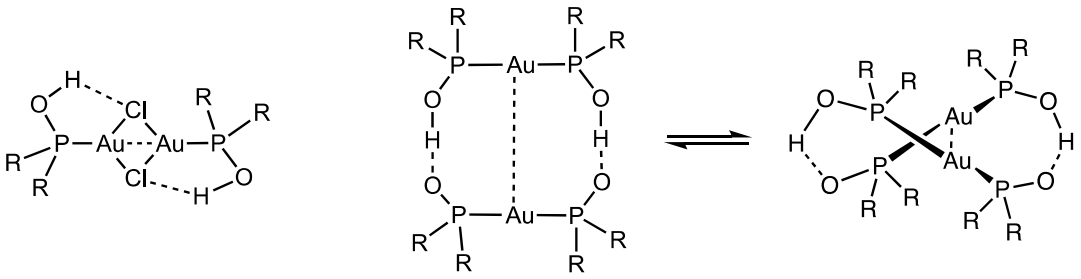
In our group we prepared the first gold complex with the optically pure, phosphine oxide (*S*)-^{t}BuMeP(O)H, which easily substituted the tht ligand when reacted with [Au(tht)Cl][192] providing Au(I) linear complex as a pale grey solid in good yield (Scheme 78).



Scheme 78. Synthesis of the optically pure Au(I) complex.

Crystals of this complex contained three molecules in the asymmetric unit with very similar distances and angles.

In the literature Au-SPO complexes present symmetric dimeric structures with the gold centres stabilised by aurophilic interactions and interconnected by two terminal O-H···Cl hydrogen bonds.[191] (Scheme 79)



Scheme 79. Aurophilic interactions in Au(I) SPO complexes.

In solution, it has been found that, in the case of disubstituted Au(I)SPO complexes (Scheme 79), the dimeric structures are in dynamic exchange according to NMR, where there is no rupture of O–H---O hydrogen bonds or Au---Au interactions, inducing only conformational changes in the molecule. The nature of these interactions has been found to have an influence in some catalytic reactions.[190,191]

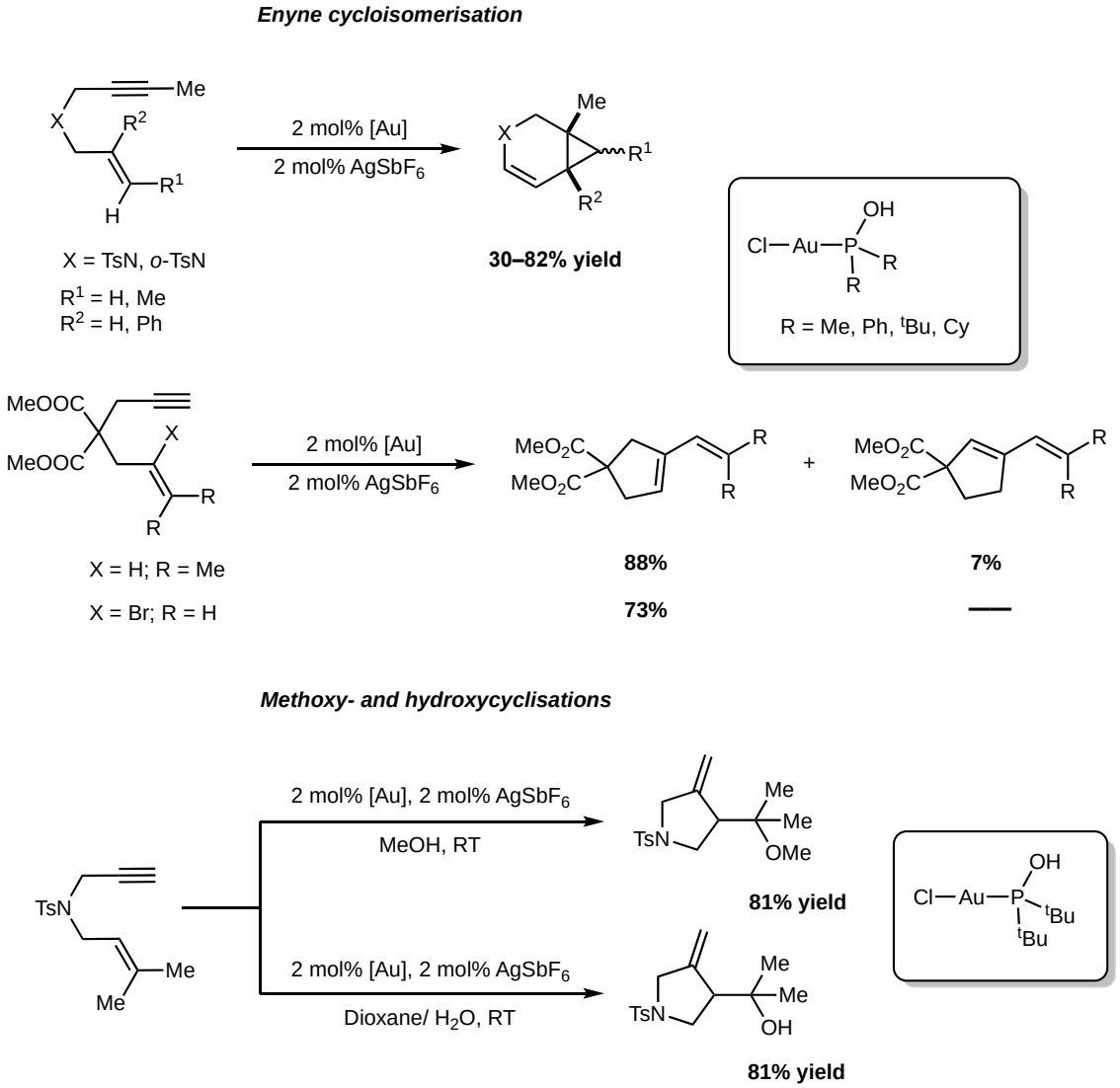
5. Non-enantioselective catalysis

The prodigious utility of phosphines and other trivalent derivatives in homogeneous catalysis is somewhat shadowed by their air-sensitivity, due to stability of the phosphoryl group (P=O) in pentavalent phosphorus compounds. SPOs turn this weakness into strength and for this reason are very interesting in catalysis with the hope to avoid the sophisticated and expensive air-free conditions that traditional catalysis require.

Since 1986 when van Leeuwen and co-workers reported the first application of SPOs on the Pt-catalysed hydroformylation of olefins,[5] the use of these systems have gained great interest. A summary of the main applications of SPOs in this field is presented through the following sections.

5.1. Isomerisations and rearrangements

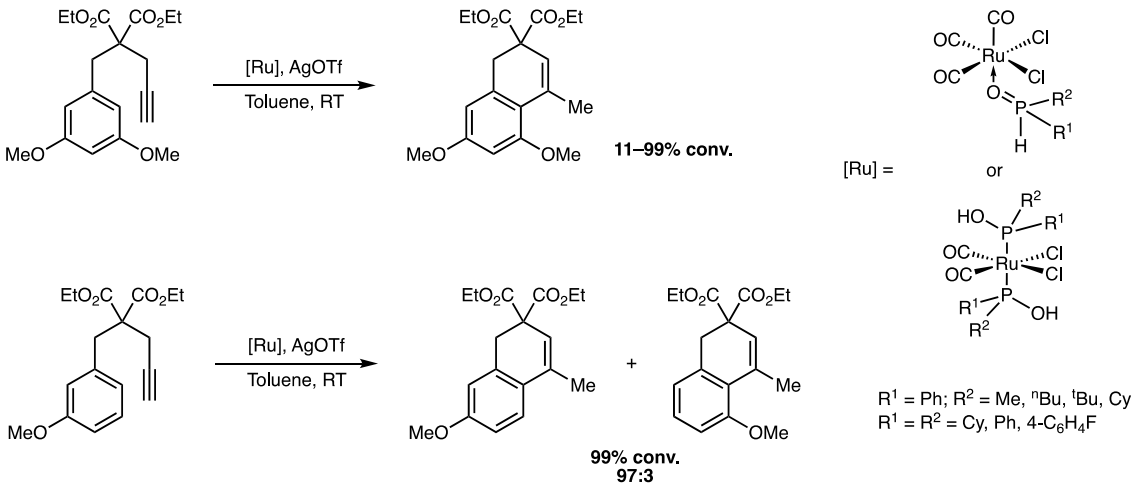
A few years ago, Fensterbank and coworkers[191] described that SPO-Au(I) complexes (Scheme 79) were active in enyne cycloisomerisation and hydroxyl- and methoxycyclisation reactions (Scheme 80).



Scheme 80. Au/SPO-catalysed reactions involving enynes.

The complex [ClAu(P*t*BuPhOH)] displayed good activities in the cycloisomerisation of several enynes under mild conditions, even with deactivated substrates. In the same paper, the same complex is used in a few hydroxy- and methoxycyclisations.

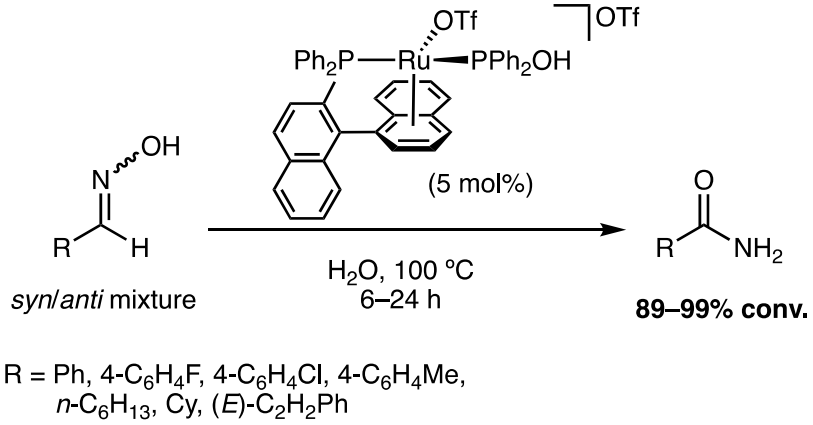
Slightly later, Buono, Clavier and coworkers[81] reported the use of carbonyl Ru-SPO complexes (Scheme 25) in the cycloisomerisation of arenynes (Scheme 81).



Scheme 81. Ru-catalysed cycloisomerisation of arenynes.

They found that the dimeric precursor [{RuCl(μ-Cl)(CO)$_3$}$_2$] with silver triflate was inactive in the transformation in contrast to the complexes with SPO ligands. The best results were obtained with the most electron-rich ligands, such as dicyclohexylphosphine oxide.

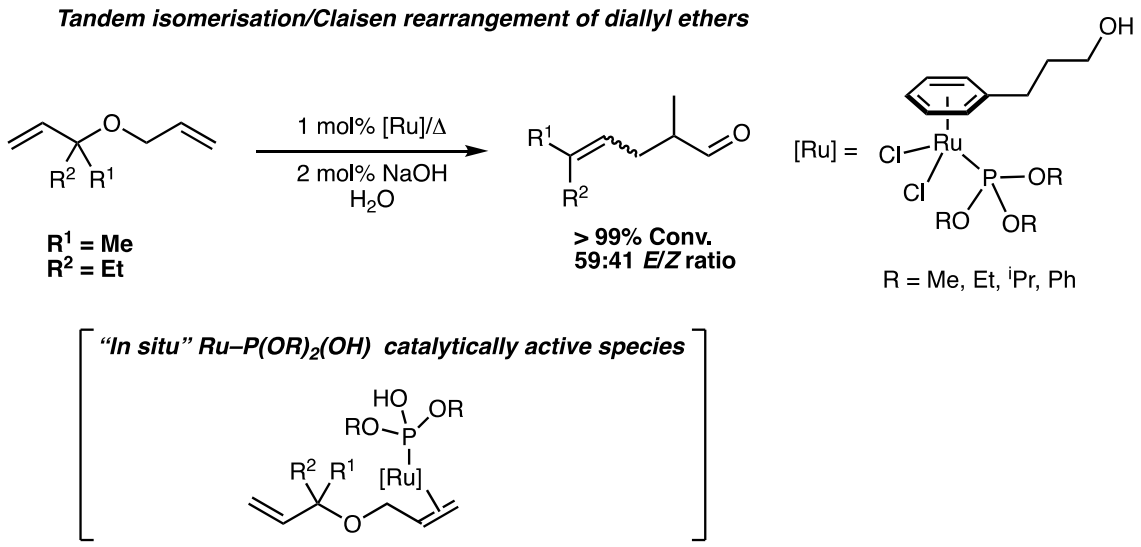
An interesting reaction is the rearrangement of aldoximes to amides (Scheme 82), catalysed by the tethered ruthenium(II) complex of Scheme 21.[193]



Scheme 82. Rearrangement of aldoximes into amides catalysed by a Ru complex.

This reaction is an atom economical process to obtain primary amides that involves a dehydration/rehydration sequence via the nitrile intermediate.[194] The aldoximes were completely rearranged with 5 mol% of the catalyst in neat water at 100 ºC. The mechanism of the reaction is basically the same that the nitrile hydration and will be discussed later. Indeed, the same complex and many other Ru complexes have been found to be excellent catalysts for the hydration of nitriles.[13,195]

Recently, Crochet, Cadierno and coworkers[196] described the tandem isomerisation/Claisen rearrangement of diallyl ethers in aqueous sodium hydroxide solution, to yield α,β-unsaturated aldehydes, catalysed by [$RuCl_2(\eta^6$-arene$)(PR_3)$] complexes (Scheme 83).

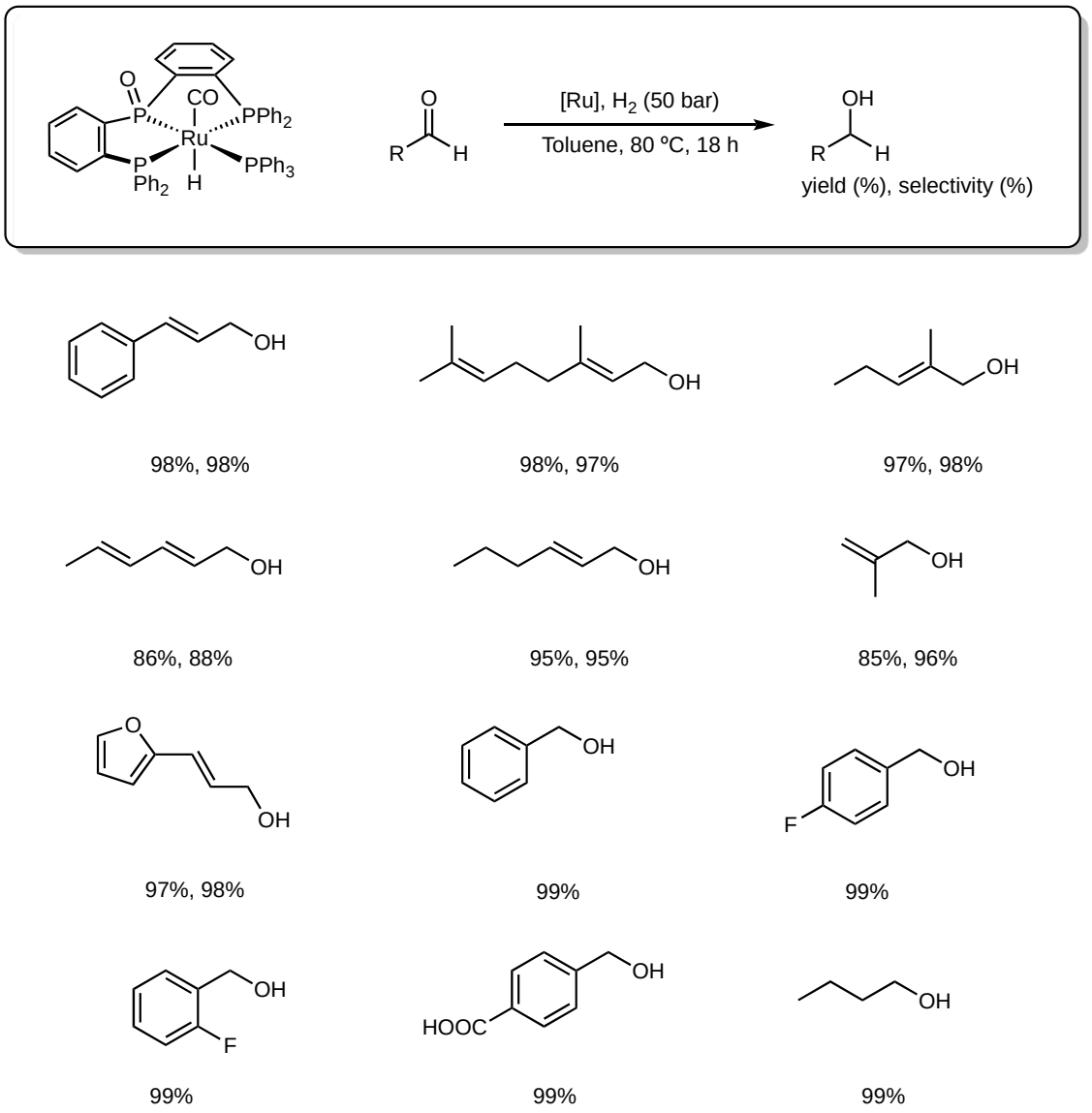


Scheme 83. Ru-catalysed tandem isomerisation/Claisen rearrangement of diallyl ethers.

They used several phosphines and phosphites, but they found that the best results were obtained with triethylphosphite. After some mechanistic studies, they concluded that one of the ethoxy groups of the triethylphosphite readily hydrolyses generating diethylphosphite-Ru species (a HASPO) that facilitates the first isomerisation step.

5.2. Hydrogenation

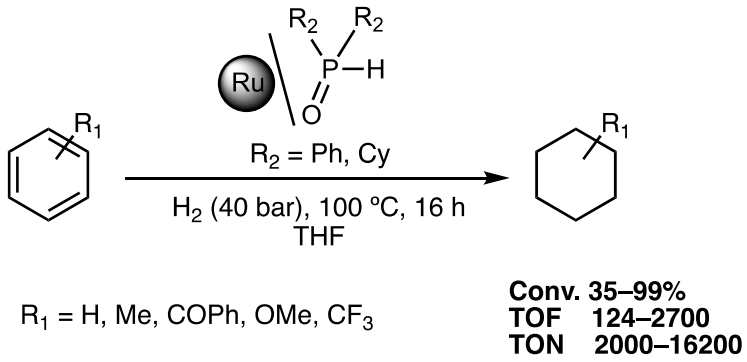
There are also some applications of Ru-SPO complexes in hydrogenation. Focusing on non-enantioselective reactions, Zhang and coworkers[197] recently described a tridentate diphosphine-SPO ligand that formed a very stable Ru(II) hydride complex, containing a molecule of carbon monoxide. This complex was very active in the hydrogenation of aldehydes and ketones (Scheme 84).



Scheme 84. Hydrogenation of aldehydes by a tridentate diphosphine-SPO ligand.

The complex is especially suited for the selective hydrogenation of α,β-unsaturated aldehydes, because leaves the olefin untouched (TON up to 36500 and 99% of selectivity). Some mechanistic studies revealed that an outer-sphere mechanism was operative, with the formation of a phosphinous-acid dihydride intermediate.

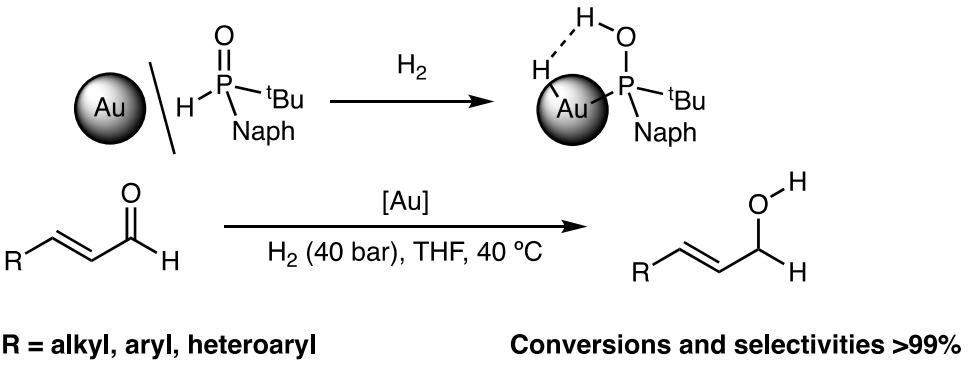
As already stated, in recent years SPOs are finding increased used in the stabilisation of nanoparticles (NPs)[87] and in this line the first applications of these systems are being reported. In the case of hydrogenation, van Leeuwen and coworkers[198] prepared Ru nanoparticles and used them in the hydrogenation of substituted benzenes (Scheme 85).



Scheme 85. Hydrogenation of aromatic hydrocarbons by SPO-stabilised NPs.

They used several SPOs with different electronic and steric properties and were able to obtain NPs with a narrow size distribution. The nanoparticles with the diphenylphosphine oxide were used in hydrogenation reactions of substituted benzenes to the corresponding cyclohexanes in high conversions, often in neat substrate.

Van Leewen and coworkers[189] have also reported the use of *t*-Bu(1-naphthyl)P(O)H-stabilised gold NPs (Scheme 77) in the homogeneous hydrogenation of substituted aldehydes (Scheme 86).

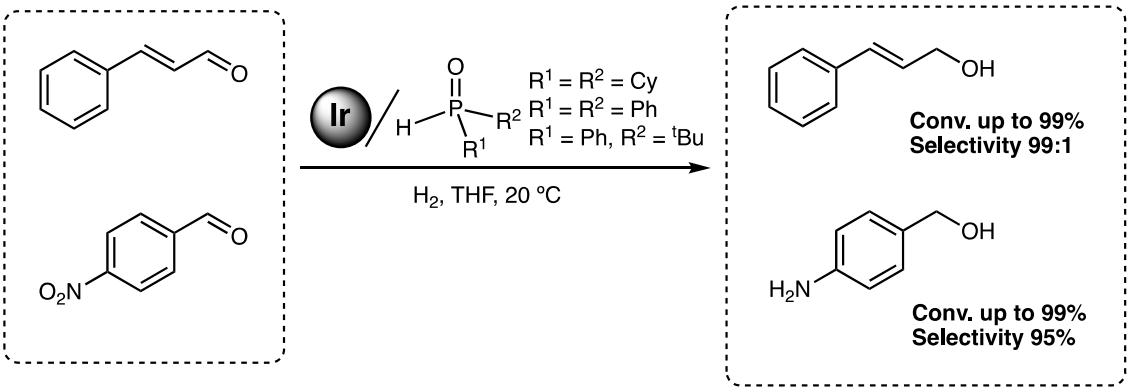


Scheme 86. Hydrogenation of functionalised aldehydes.

This was the first application of Au/SPO systems in homogeneous catalysis.[191] The reaction was remarkably chemoselective and α,β-unsaturated aldehydes were reduced to the alcohols without affecting the C–C double bond. An important example of this transformation was the smooth reduction of acrolein to allyl alcohol. The same exclusive reduction of the carbonyl group in aldehydes bearing cyano, nitro, alkynes other groups usually sensitive to hydrogenation was observed. Interestingly, other Au-NPs stabilised by ligands different from SPOs were completely inactive in aldehyde reduction. Shortly after this report, the same group extended this study to a small library of SPOs.[190] They demonstrated that aryl-substituted SPOs presented a strong

polarity of the P=O bond and showed a high catalytic activity and almost perfect chemoselectivity in the hydrogenation of substituted aldehydes. In contrast, alkyl-substituted SPOs exhibit lower polarity of the phosphoryl bond or the presence of P–OH bonds, slowing the heterolytic cleavage of hydrogen and thus worsening the catalytic results. The perfect chemoselectivity can be explained by ligand-metal cooperative effects, in which the SPO ligand plays a crucial role. Hence by means of DFT calculations[199] it has been recently found that the SPO provide an effective Frustrated Lewis Pair that allows the heterolytic activation of the dihydrogen molecule, which is then added to the aldehyde carbonyl group through a concerted mechanism.

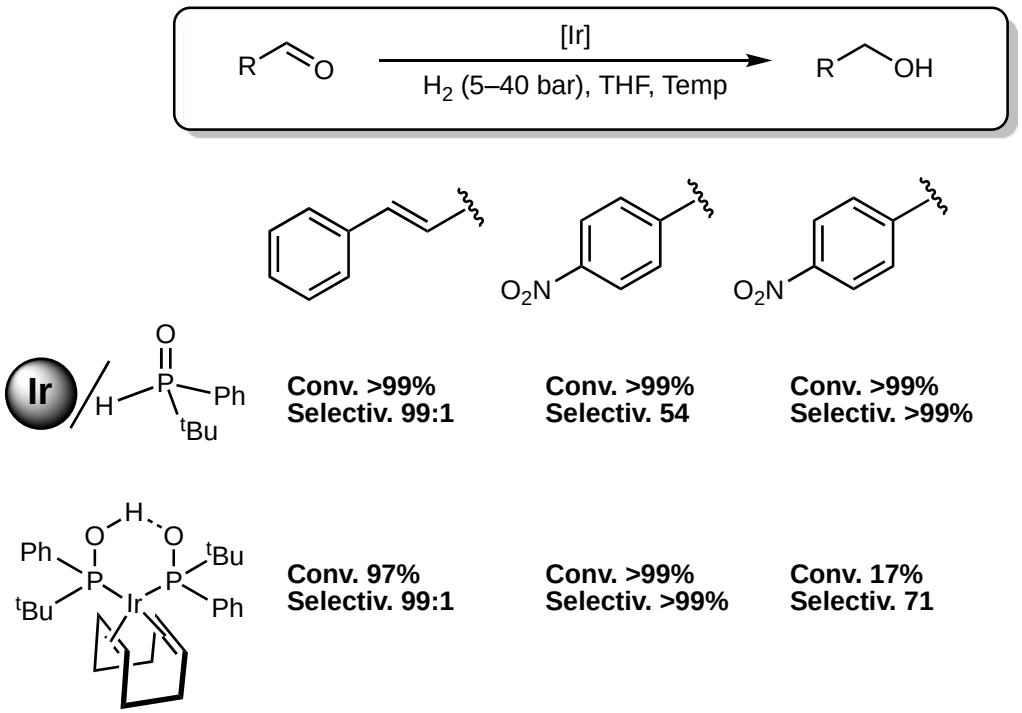
Recently the group of van Leeuwen has also been active in the development of Ir/SPO systems for hydrogenation. In a first study they used Ir NPs, stabilised with three different SPOs, $Ph_2P(O)H$, $Cy_2P(O)H$ and $^tBuPhP(O)H$, for the hydrogenation of cinnamaldehyde and *p*-nitrobenzaldehyde (Scheme 87).[82]



Scheme 87. Ir/SPO-hydrogenation of aldehydes.

Once again, the Ir-NPs were very chemoselective towards the reduction de carbonyl of the aldehydes in THF at RT. It was found that the NPs stabilised with *t*BuPhP(O)H were both the smallest and the most active but very little ligand effect was found. In the case of the hydrogenation of *p*-nitrobenzaldehyde, concomitant reduction of the nitro group to the give the aniline was observed.

In parallel, the same group[133] reported a study in which they compared the catalytic activity of a molecular Ir-SPO complex (Scheme 45) and Ir NPs stabilised with the same SPO, namely $^tBuPhP(O)H$ (Scheme 88).



Scheme 88. Ir/SPO-hydrogenation of aldehydes.

These two Ir-SPO catalysts showed markedly distinct rates and selectivities in the hydrogenation of substituted aldehydes. The Ir-SPO complex showed very high activity and selectivity in the hydrogenation of cinnamaldehyde and *p*-nitrobenzaldehyde. The Ir/SPO-NPs were less active but more robust than the complex giving high selectivities in the hydrogenation of substrates that poison the molecular catalyst. Very recently, the same group expanded the studies[134] on the catalytic potential of the Ir-SPO complex of Scheme 45. They found that it is an excellent catalyst for the hydrogenation of substituted aldehydes, displaying high activities and selectivities for a wide variety of substrates, with TOF values up to 2040 h^{-1} without the need of bases or additives. The catalysis presumably operates though a ligand-metal cooperative mechanism in which the SPO plays a double role as a modifying ligand and as a functional ligand, acting as heterolytic activator of the H_2 molecule.

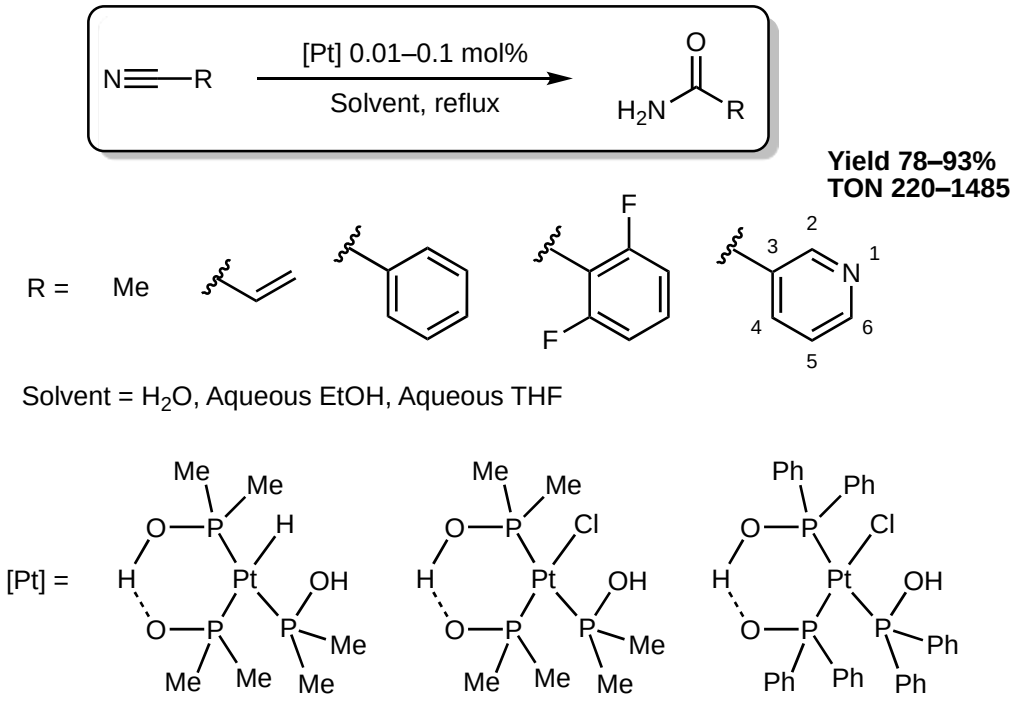
5.3. Transfer hydrogenation

There dimeric Rh(III)-SPO complexes of Scheme 39 were employed[130] in transfer hydrogenation of ketones. Under the optimal conditions, acetophenone was reduced with a 92% conversion and a TOF of 1825 h^{-1}. The Rh:SPO ratio was found to be crucial to obtain a good catalytic activity and had to be adjusted for every substrate. DFT calculations were used to characterise several intermediates and show that the

process occurs via a concerted outer-sphere mechanism. When a binaphthol-derived phosphorous acid was employed, up to 89% *ee* was obtained in the reduction of acetophenone.

5.4. Nitrile hydration

The acid- or base-catalysed hydrolysis of nitriles to amides is an atom-economical organic transformation but as it requires harsh conditions it has the drawback that often the amide is further hydrolysed to the acid. To have better selectivity, transition-metal catalysis is advantageous and SPO ligands seem to be particularly fit for this reaction.[200,201] The first use of SPOs in this area was a communication quite some time ago by Parkins and Ghaffar,[178,202] who employed platinum complexes of simple monophosphorus ligands in nitrile hydrolysis (Scheme 89).

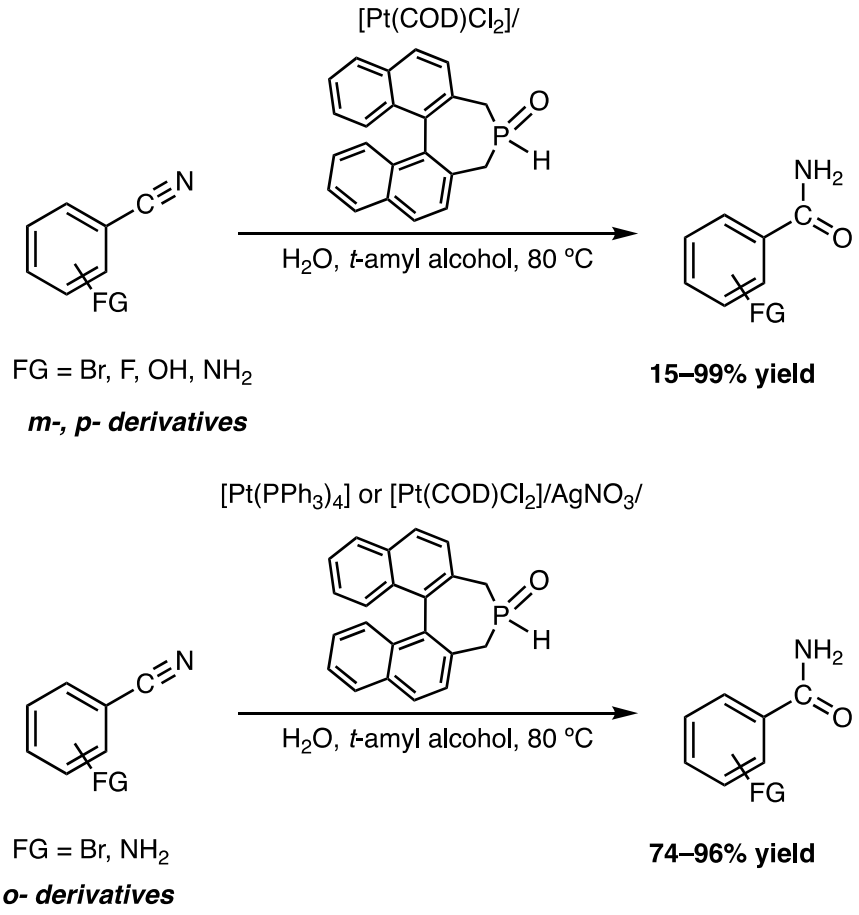


Scheme 89. Hydrolysis of nitriles catalysed by Pt-SPO complexes.

They found that the most active system was with dimethylphosphine oxide in aqueous solutions and proposed a mechanism in which the carbon of the coordinated nitrile is attacked by the hydroxyl group of the phosphinous acid to explain the high activity of SPOs compared to tertiary phosphines. With this system a wide range of nitriles could be hydrated under relatively mild conditions, sometimes in pure water.[179,203] For these reason the catalyst [PtH{$(PMe_2O)_2H$}(PMe_2OH)], known as the Parkin catalyst, has

been used in the synthesis of a number of complex organic molecules[13,201,204] and has merited its own review, written a few years ago by Cadierno.[205]

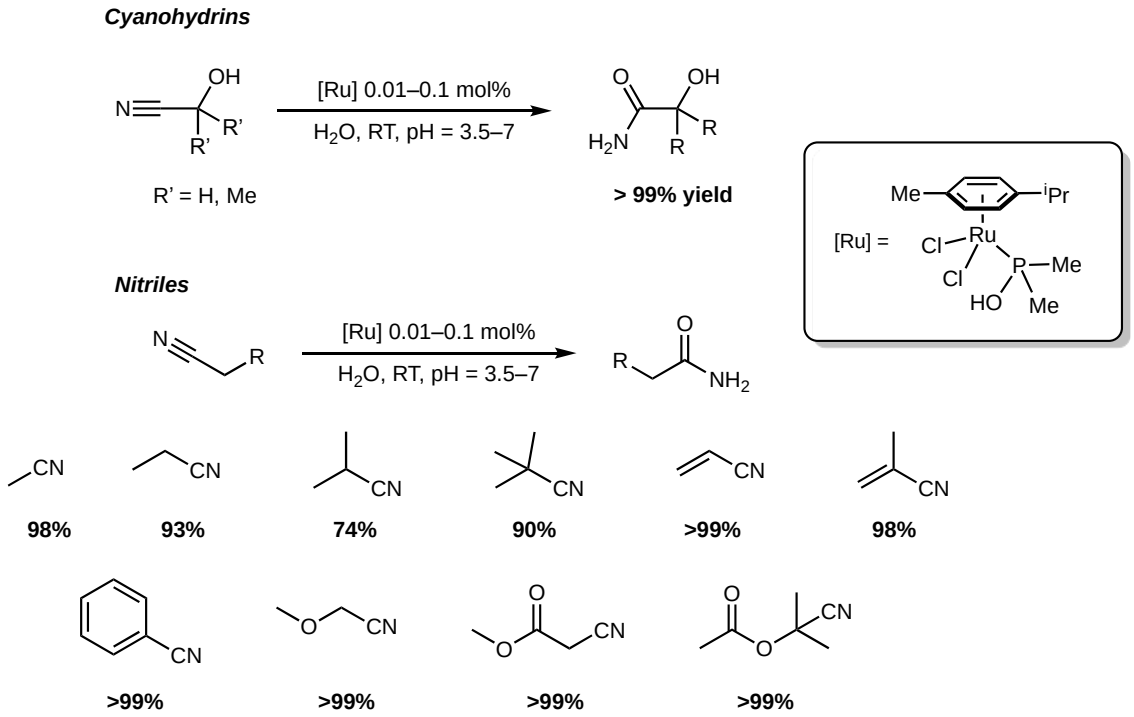
Pt(II) complexes bearing a chiral SPO ligand (Scheme 68) have been applied to the hydration of aromatic nitriles by van Leeuwen and coworkers (Scheme 90).[180]



Scheme 90. Pt/SPO-catalysed hydration of aromatic nitriles into carboxamides.

The $[Pt(SPO)_3Cl]Cl$ complex (Scheme 68) showed moderate activity in the hydration of *m*- and *p*-substituted benzonitriles and were totally inactive in the hydration of *o*-substituted derivatives. In contrast, the hydride complex formed by the reaction of the SPO and $[Pt(PPh_3)_4]$ and the cationic complex derived from $[Pt(SPO)_3Cl]Cl$ by chloride extraction resulted to be much more active for many benzonitriles, including the *ortho*-substituted ones.

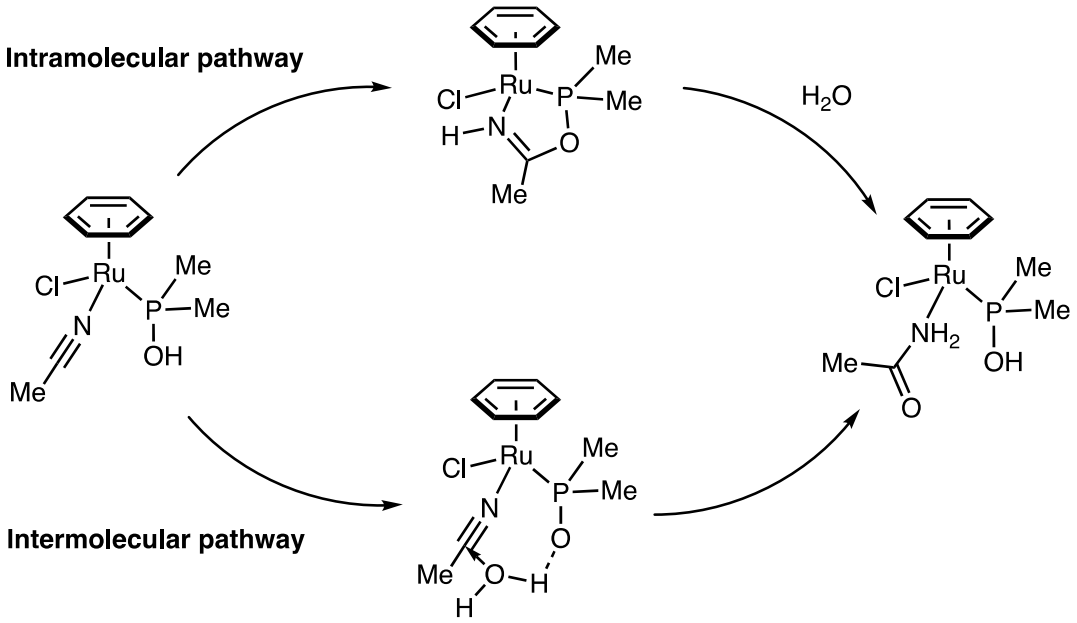
Despite the above results, most of the work has been carried out by using ruthenium(II) complexes[13,195] since the first report of Tyler and coworkers a few years ago,[104] (Figure 6) who employed the same dimethylphosphinous acid as a ligand to Ru-*p*-cymene (Scheme 91).



Scheme 91. Hydrolysis of nitriles catalysed by a Ru-*p*-cymene-PMe_2OH complex.

This SPO was faster than other phosphorus ligands with hydrogen bond accepting capability and was able to hydrate many nitriles in water under neutral conditions. An interesting aspect of this type of catalysts is that they are capable of hydrating cyanohydrins at ambient temperature, which is a challenge because they are prone to decompose to HCN that would poison the catalyst.[179,206,207]

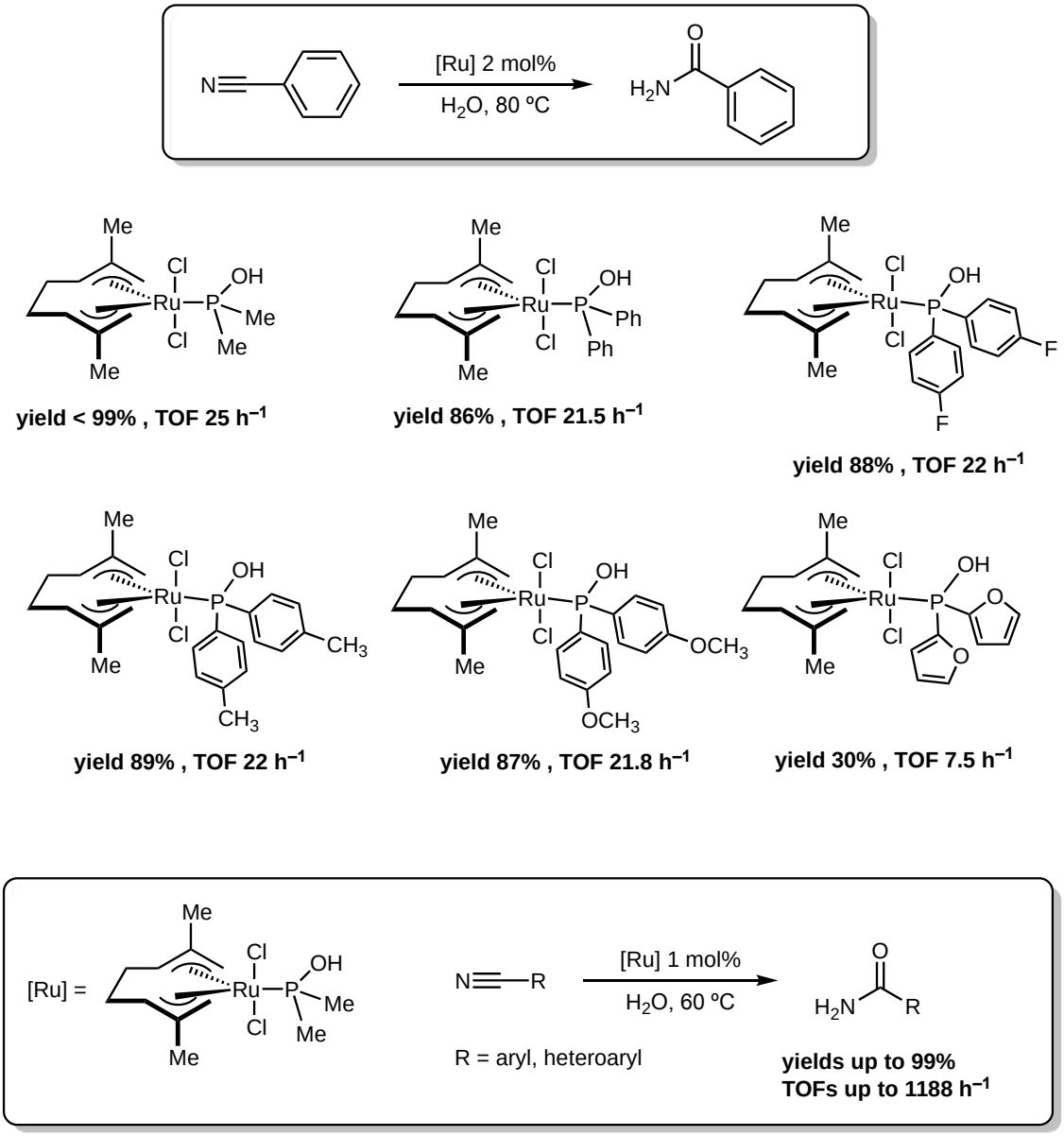
These studies were extended to many Ru(II)-arene complexes with SPOs and related phosphorus acid ligands by Cadierno and coworkers,[105] (Figure 6) who found that the most active systems where again those based on dimethylphosphinous acid, achieving TOFs up to 32 h^{-1} at 100 ºC. In addition, they performed calculations on the mechanism of the reaction by DFT and showed that the SPO ligand played a key role in the hydration process by the formation of a metallacycle (Scheme 92).



Scheme 92. Involvement of the SPO in the Ru-catalysed hydration of nitriles.

They found that the hydration reaction does not proceed by direct addition of water to the coordinated nitrile but via a five-membered metallacycle formed by intramolecular attack of the phosphinous acid to the nitrile. The hydrolysis of this metallacycle liberates the amide product and regenerates the catalyst.

The same simple SPOs have been also been tested with bis(allyl)ruthenium(IV) complexes (Scheme 30) by the same authors, with very good results (Scheme 93).[113,114]

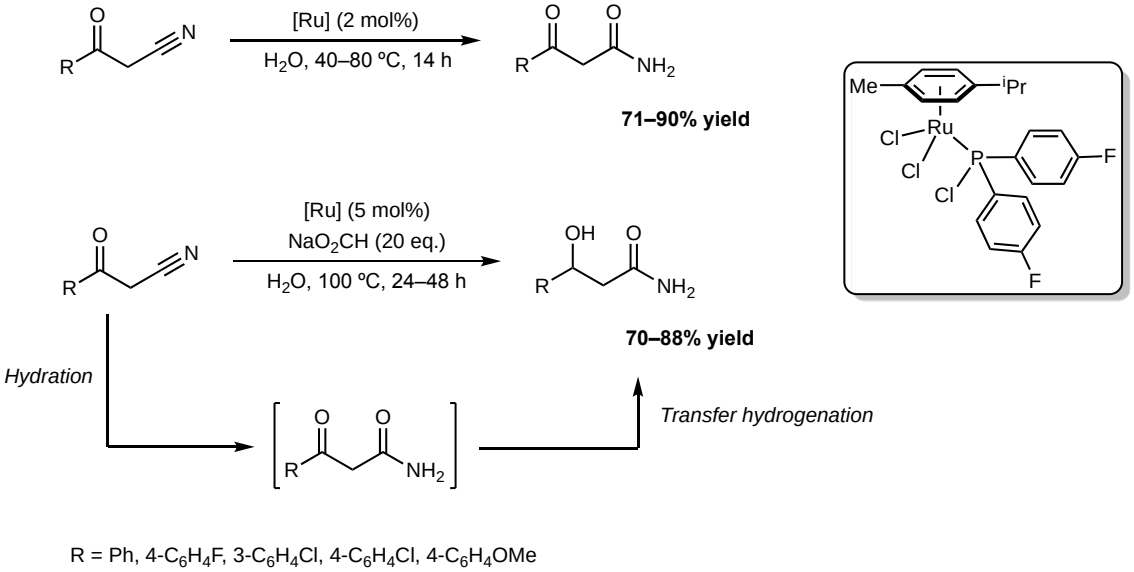


Scheme 93. Hydration of nitriles by Ru(IV)-bis(allyl) complexes.

The reactions can be quickly performed in neat water without any additive and proceed smoothly for a large variety of nitriles giving the corresponding primary amides. The presence of many functional groups in the nitrile is well tolerated, highlighting the high chemoselectivity of the catalytic system. The elevated activity is possibly due to the high solubility and stability of the systems in water. Indeed, after selective crystallisation of the amide product, the Ru catalyst remains completely dissolved and can be reused. The good properties of the system were used to synthesise some pharmacologically important compounds as well as in the hydration cyanohydrins.

At this point it has to be recalled that ruthenium-phosphinous acid complexes can be prepared by hydrolysis of the coordinated chlorophosphines (Scheme 22 and Scheme

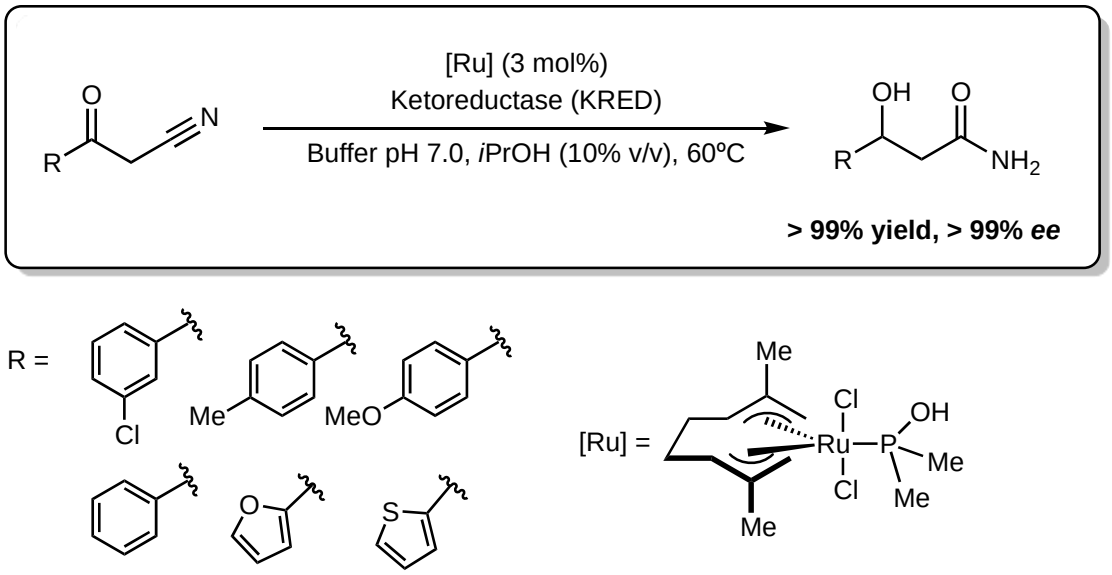
30). Hence as the nitrile hydration reactions take place in water, the latter precursors can be directly used because they easily generate the desired Ru-SPO compounds under catalytic conditions. This has been demonstrated both for the Ru(II)-arene[107] and Ru(IV)-bis(allyl)[114] complexes. An example of the utility of in-situ generated Ru(II)-arene-SPO complexes is in the hydration of β-ketonitriles to β-ketoamides (Scheme 94), whose precedents required the use of enzymes such as nitrile hydratases.[13]



Scheme 94. Catalytic synthesis of β-ketoamides and β-hydroxyamides from β-ketonitriles.

This well-known ability of Ru(II) complexes to catalyse the transfer hydrogenation (TH) reactions was used to develop a useful tandem hydration/TH reaction allowed the direct conversion of β-ketonitriles to β-hydroxyamides with a Ru(II)-*p*-cymene SPO complex with sodium formate in water.[208] Interestingly the reactions had to be performed under slightly harsher conditions and with a higher catalyst loading compared to the hydration of nitriles since the reduction of the ketone was found to be the rate-determining step.

The exact same transformation has been recently reported by the same authors using the Ru(IV)-bis(allyl)-SPO complex for the nitrile hydration reaction followed by an enzymatic reduction with ketoreductases, in a tandem hydration/bioreduction process (Scheme 95).[209]



Scheme 95. Tandem nitrile hydration/bioreduction reaction to yield β-hydroxyamides from β-ketonitriles.

This process took place in aqueous phosphate buffer in high yields and with very high enantioselectivities. It should be noted that the enantioselectivity is obviously imparted by the enzyme and for this reason this reaction is not included in the enantioselective catalysis part. This reaction nicely illustrates the possibility to combine classic transition-metal catalysis with enzymatic catalysis.

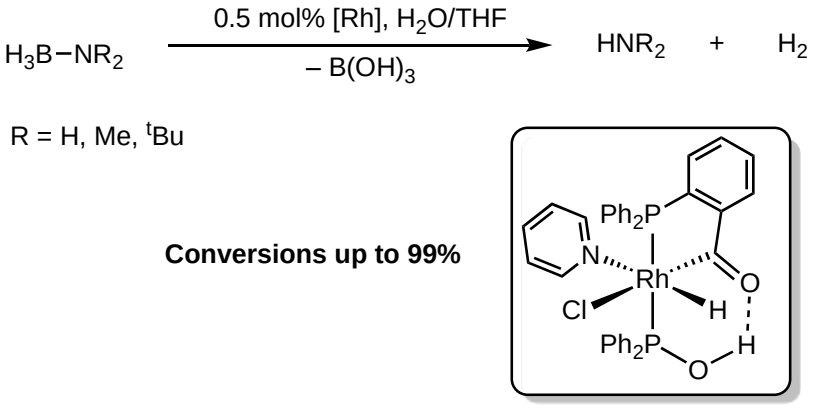
Other Ru-SPO complexes have been found to be active in the hydration of nitriles, such as the cationic tethered complexes of Scheme 21 but with poorer results compared to the neutral Ru(II) and Ru(IV) complexes just described. In this case however, they were found to be active in the rearrangement of aldoximes to primary amides,[193] as discussed earlier.

The related Os-SPO complexes have been much less explored in the hydration of nitriles and the existing studies have been carried out with [Os(η^6-*p*-cymene)(PR_2OH)] complexes (Scheme 31).[116] Like their Ru counterparts, they are competent catalysts in nitrile hydration in pure water without need of any additive and are thought to follow the same mechanism with the cyclic five-membered intermediate. The most active system is again with the dimethylphosphinous acid. This compound is very active and chemoselective and for the less reactive aliphatic nitriles is superior to its Ru analogue. It seems that this better performance is due to subtle differences in the ring strain of the Os intermediate metallacycle. Finally, it should be mentioned that in parallel to the Ru analogues, the catalytically active Os(II)-arene SPO complexes can be prepared by *in-situ* P–Cl hydrolysis of the parent complexes with coordinated chlorophosphines.[116]

Interestingly, however, they could also be prepared by P–N bond hydrolysis of complexes with a coordinated aminophosphine.[117]

5.5. Hydrolysis of amine-boranes

A report from Garralda and coworkers (Scheme 41) [131] described the synthesis of rhodium(III) acylphosphine-hydrides stabilised by intramolecular H bonds involving a coordinated SPO, which catalysed the hydrolysis of amine-boranes (Scheme 96).



Scheme 96. Hydrolysis of amine-boranes catalysed by Rh(III)/SPO-complexes.

The complexes were evaluated in the hydrolysis of amine-boranes to release hydrogen, a very interesting reaction in hydrogen storage applications. The reaction occurred under mild conditions (40 ºC) with low catalyst loading and it could be easily reused.

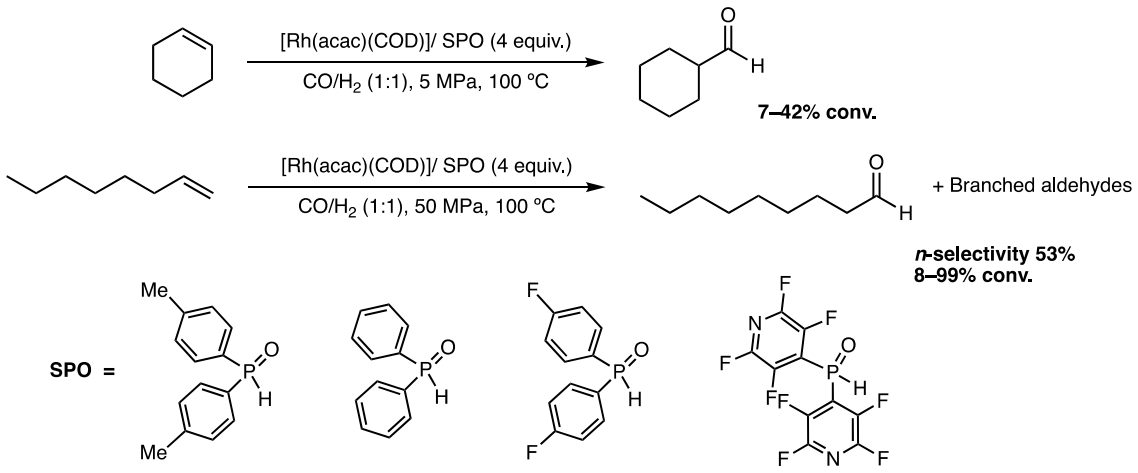
5.6. Hydroformylation

The hydroformylation of olefins is an extremely important reaction, especially industrially. As early as 1983 Matsumoto and Tamura[123] applied diphenyl- and dioctylphosphine oxide in the Rh-catalysed hydroformylation of linear olefins. Although they used triphenylphosphine as ligand, the addition of the mentioned phosphine oxides increased the stability of the catalyst, probably by formation of $[Rh_2(CO)_2(PPh_3)_2(R_2P(O))_2]$.

A few years later, van Leeuwen and coworkers[5] reported that Pt/SPO hydride complexes (Scheme 67) catalysed the hydroformylation of 1- and 2-heptene yielding linear aldehydes (along with some alcohols) with a 90 and 60% selectivity, respectively. In further studies, several alkyl and acyl intermediates could be identified[210] and it was concluded that diphenylphosphinous acid was an interesting ligand with peculiar

properties, capable of activating the hydrogen, which seems to be the bottleneck of in Pt-catalysed hydroformylation.[211] It has to be noted that prolonged hydroformylation produces inactive dimeric Pt complexes containing a phosphido and a hydrido bridge.[210]

Much more recently, Börner and coworkers[212] revisited the Rh/SPO-catalysed hydroformylation. They used diphenylphosphine oxide and three other diarylphosphines oxides with electron-poor aryl groups for the hydroformylation of 1-octene and cyclohexene (Scheme 97).



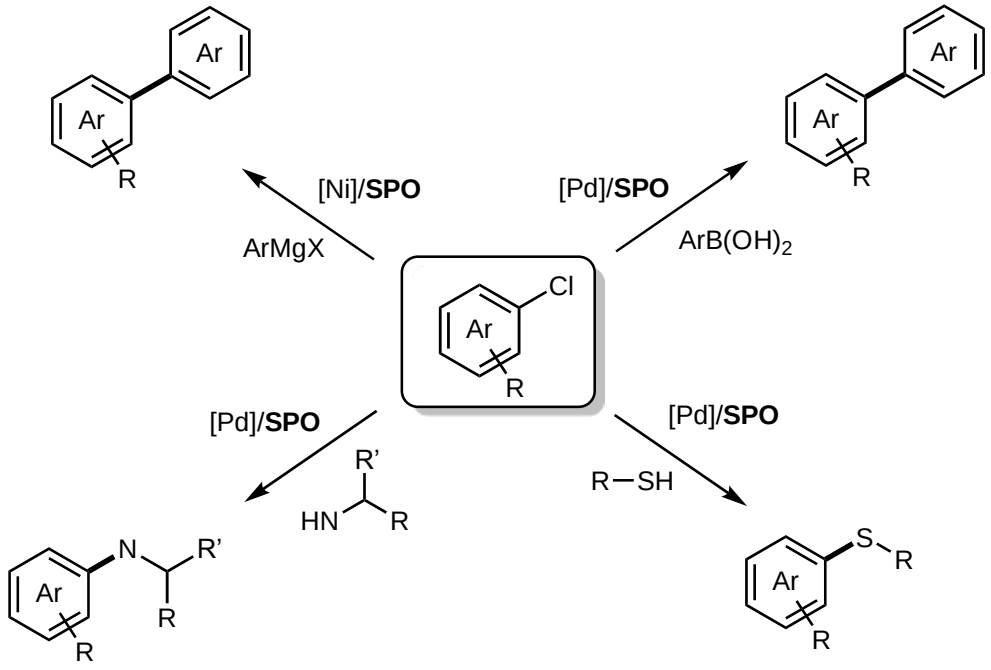
Scheme 97. Rh/SPO-catalysed hydroformylation.

The four SPOs performed better than the typically used triphenylphosphine although rather low *n*-selectivities were observed. Interestingly, methanol and other protic solvents gave better results, as they preserve the *bidentate* coordination mode.[126] The same authors[33] extended the study of the Rh/HASPO-catalysed hydroformylation, in the context of the study of the degradation/hydrolysis of several phosphites used in industrial hydroformylation.[213] The results were poorer than with the SPOs just described and in addition a side reaction involving the originated aldehydes generated α-hydroxyphosphonic acid diesters, reducing the concentration of ligand and hence the activity of the resulting catalysts.

5.7. Cross-coupling

The most important application of SPOs in homogeneous catalysis is their use in Pd-catalysed coupling reactions. The first reports of the area are due to Li and coworkers at DuPont and date back to 2001.[30,156] They showed that the Pd-SPO complexes mentioned before (particularly di(*tert*-butyl)phosphine oxide) were excellent ligands for a variety of cross-coupling reactions with vinyl and aryl chlorides, including Suzuki-

Miyaura, Mizoroki-Heck, Buchwald-Hartwig aminations and related reactions. In addition, SPOs with nickel were also active in Kumada-Tamao-Corriu reactions (Scheme 98).



Scheme 98. Pd/SPO- and Ni/SPO-catalysed cross-coupling reactions of aryl chlorides.

This is a remarkable result, because aryl chlorides are rather inert substrates for cross-coupling reactions that usually require air-sensitive trialkyl- or dialky(2-biphenylyl)phosphines. The success of SPOs in these reactions was attributed to the formation of electron-rich anionic species in the basic media under catalytic conditions, facilitating the rate-limiting oxidative addition of inactivated aryl chlorides to Pd(0) precursors.

These results spurred a fruitful research in Pd-catalysed (and also Ni-catalysed) cross-couplings: Suzuki-Miyaura couplings[35,172,174,214-219] but Mizoroki-Heck,[157,159,175,220-222] Stille,[157,223] Sonogashira,[224,225] Hiyama,[226,227] Kumada-Tamao-Corriu,[31,228-230] Negishi,[155,231] and other reactions with mechanisms related to cross-coupling reactions.[155,175,225,230,232-236] In many of the cases but not all,[35,172,174,175,220-222,225,230,231,236] the ligand of choice was di(*tert*-butyl)phosphine oxide. Remarkably, some of these reactions were carried out in neat water.[11,223,224,227,234]

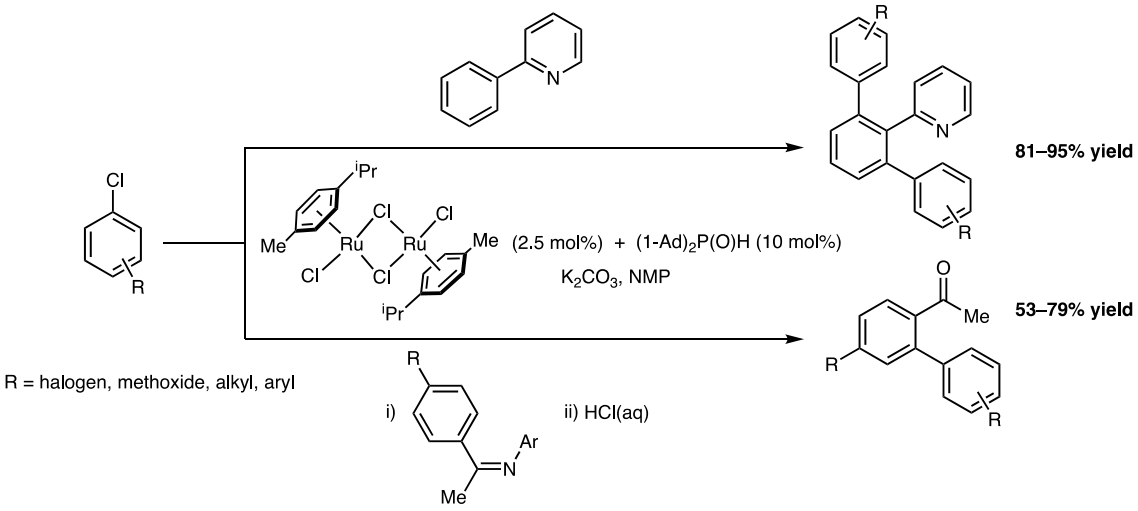
To close this section it is interesting to note the work of Bedford and coworkers,[237] who studied Suzuki-Miyaura couplings with orthometallated phosphites and phosphinites. They found that sometimes under catalytic conditions hydrolysis of the ligands generated SPOs that played a significant role on the catalytic activity, depending not only on the ligand but also on the interplay between the ligand and the palladium

precursor. It can be concluded, therefore, that as SPOs can be generated *in situ* by ligand hydrolysis they can influence the catalysis even when they are not used on purpose as ligands.

5.8. C–H bond arylation

The activation of unfunctionalised aromatic C–H bonds is a huge area of tremendous interest[238-240] that has attracted an intense research effort,[241,242] yielding a wealth of systems based on many transition metals.[243]

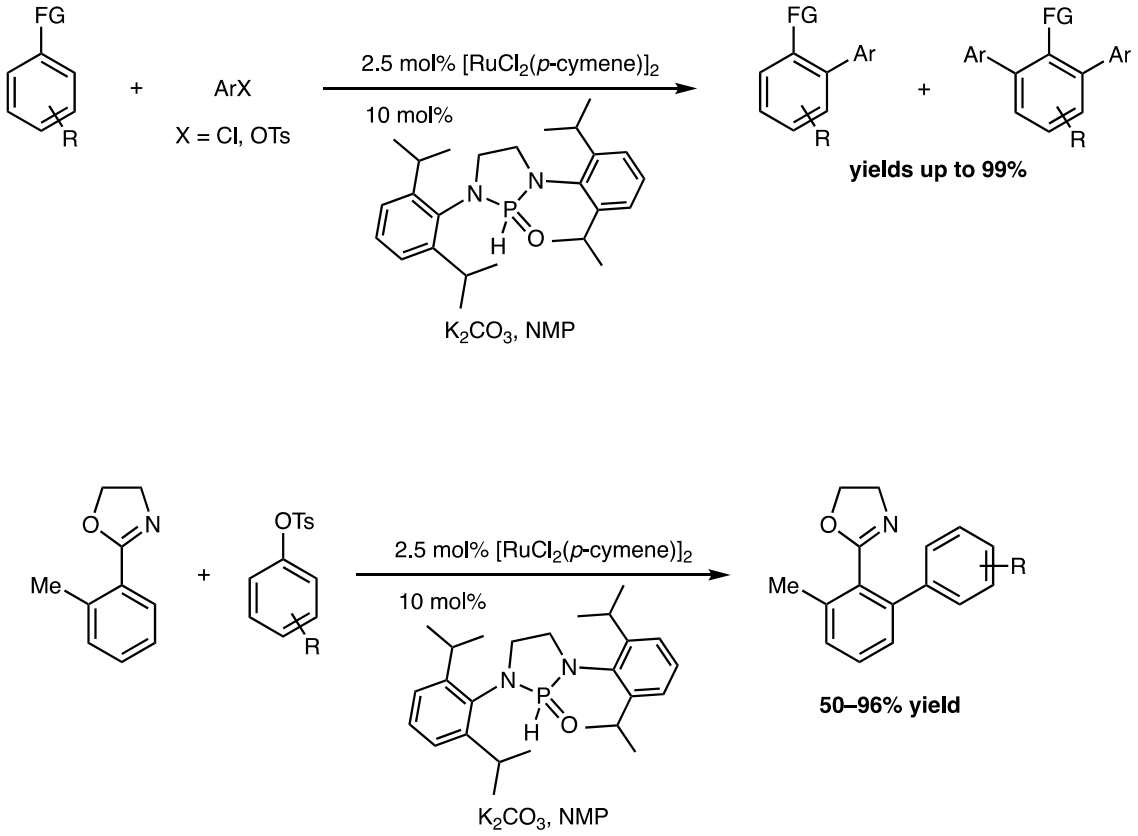
In the case of activation of C(sp^2)–H bonds, the reaction is usually known as *arylation*. In this field, the relatively inexpensive ruthenium-based systems have been profusely used[244-246] and those with SPOs so particularly successful that have merited their own reviews.[247,248] This area has advanced thanks to the research of Ackermann and coworkers, who some time ago pioneered the field with the Ru(II)-catalysed *ortho*-diarylation of 2-phenylpyridines and the monoarylation ketimines with aryl chlorides in the presence of diadamantylphosphine oxide (Scheme 99).[103,249]



Scheme 99. Ru(II)-*p*-cymene/Ad_2P(O)H-catalysed arylation reactions.

In contrast to cross-coupling reactions, this reaction was found to be quite insensitive to the nature of the aryl chloride but the reactions had to be carried out at 120 ºC to achieve high yields. The same group expanded the scope of the reaction to by arylating aryltriazoles[250] and phenoxypyridines with *p*-bromoanisole[251] although the best results were obtained when mesitylcarboxylic acid instead of diadamantylphosphine was used as ligand.[249]

When the electrophilic reagent was changed to aryl tosylates, Ackermann and coworkers[252] obtained excellent results with a very bulky diaminophosphine oxide, a HASPO (Scheme 100).

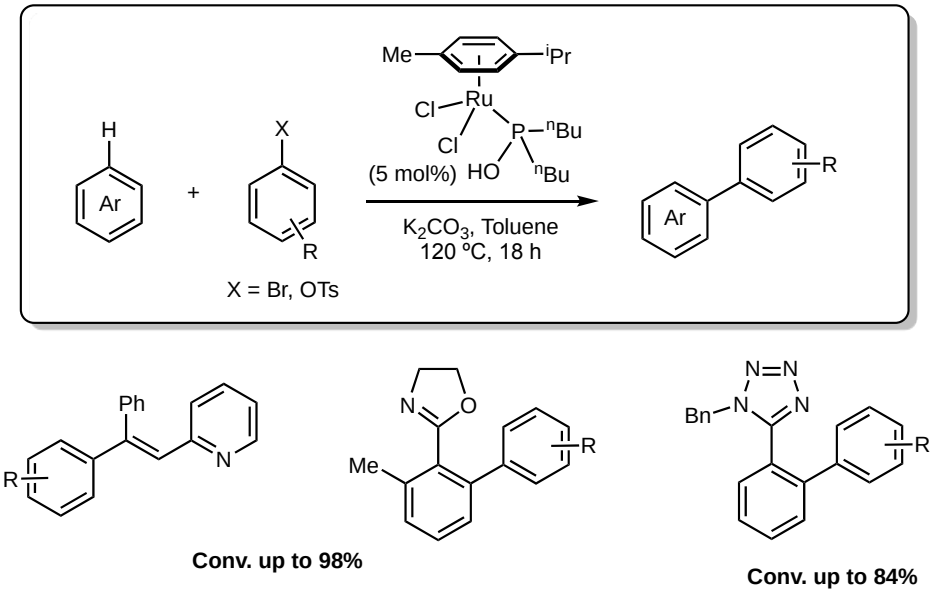


R = Me, OMe, CH=CHPh, CO_2Me, CO_2Et, CN, CF_3, COPh

Scheme 100. Ru(II)-*p*-cymene/HASPO-catalysed arylation reactions.

With this ligand, 2-phenylpyridine was almost exclusively monoarylated, in contrast to the results of Scheme 99. With the same method they also reported the arylation of *o*-tolyloxazolines. These arylations are thought to proceed through a concerted metallation/deprotonation mechanism assisted by the deprotonated SPO.

In more recent studies, Ackermann and coworkers[109] have used well-defined [$RuCl_2(\eta^6$-*p*-cymene)(PRR'OH)] acid systems (Figure 6), the same of those used in nitrile hydration, in arylation reactions. They found that the simple SPO dibutylphosphine oxide gave the best results of activity and chemoselectivity in the arylation of *o*-tolyloxazolines and 2-vinyl-pyridines with aryl bromides and tosylates (Scheme 101).



Conv. up to 98%

Conv. up to 84%

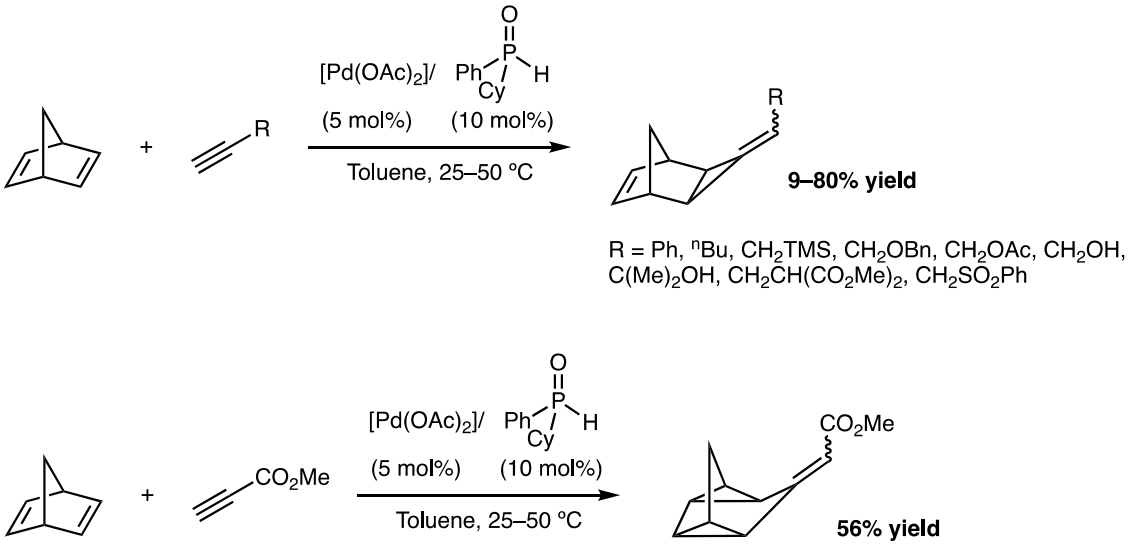
Scheme 101. Arylation reactions catalysed by well-defined Ru(II) precursors.

In addition, they showed that this chemistry is so tolerant to functional groups that can be applied to the preparation of drug precursors. At the same time, Clavier and coworkers[106] used the same type of complexes in the arylation of 2-phenypyridine with chlorobenzene and found that *t*-BuPhP(O)H was the best ligand, yielding a 89% yield in 24 h at 80 ºC. The results of the preformed catalysts outperformed those of *in situ* experiments and a marked halide effect was found.

5.9. Cycloadditions

Pd- and Pt-phosphinito-phosphinous acid complexes have been found to be excellent to catalyse [2+1] cycloadditions between norbornadienes and alkynes to afford various types of methylenecyclopropane derivatives. This chemistry has been mainly developed by Clavier and Buono, who wrote their own review on the topic.[169]

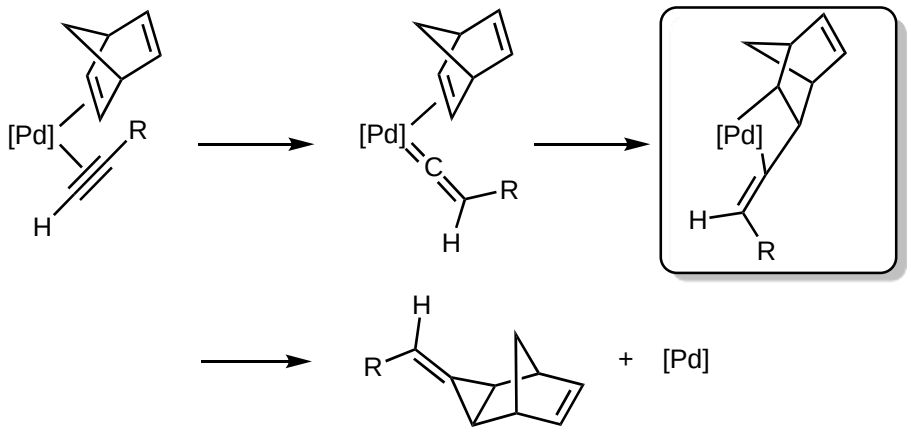
In 2005, Buono and coworkers[167] disclosed that Pd-SPO complexes that have been heavily used in cross-couplings were also active in [2+1] cycloadditions between terminal alkynes and norbornadiene, to give functionalised alkylidenecyclopropanes (Scheme 102).



Scheme 102. Pd/SPO-catalysed [2+1] cycloadditions.

This reactivity contrasts with the hydroalkynation that was observed when the well-known Herrmann-Beller phosphapalladacycle was used.[253-255] The presence of acetate rather than chloride was required for the reaction and this was attributed to the strong coordination ability of the latter. Regarding the substituents at phosphorus, in a subsequent studies[255,256] they found that CyPhP(O)H was the best SPO for the reaction, with a particularly broad spectrum of substrates, including ynamides.[257] Interestingly, it could also be confirmed that a SPO was really needed since no reaction occurred with triphenylphosphine or typical diphosphines.

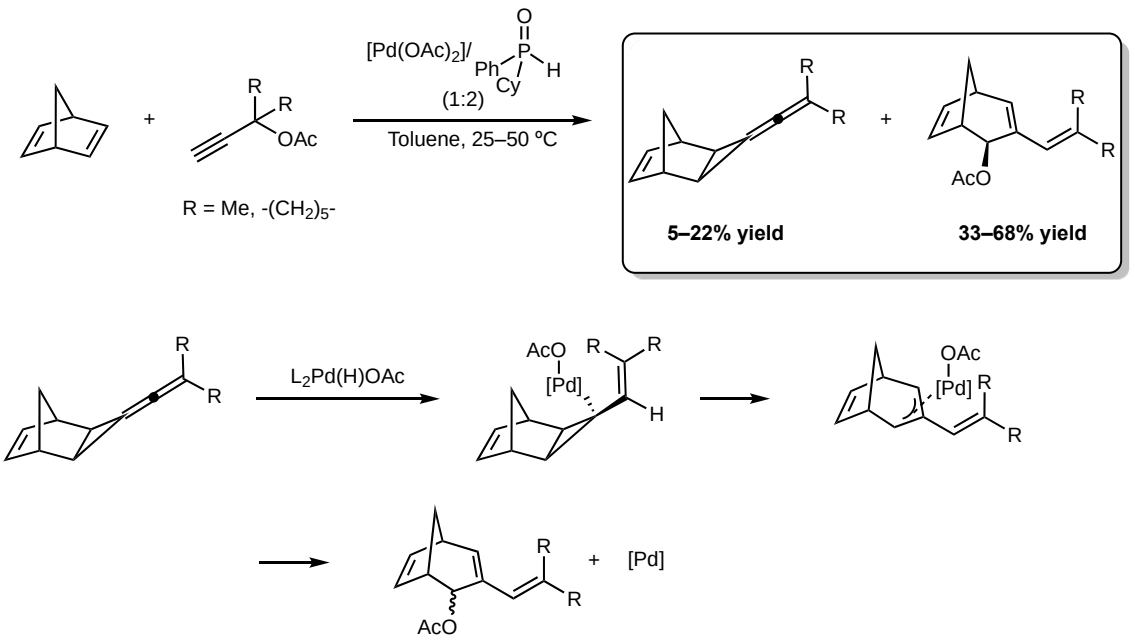
The mechanism of the reaction has been studied by experimental and computational methods[167,255,258] to ascertain why the Herrmann-Beller catalyst cleanly forms the hydroalkynation product while the SPO-based catalyst give the [2+1] cycloaddition product. It seems that in both transformation a key *syn*-carbometallated intermediate is formed that in the case of Herrmann-Beller palladacycles is rapidly hydrolysed to give the alkynation product (Scheme 103).[167,255]



Scheme 103. Key intermediates of the [2+1] cycloaddition of norbornadienes and alkynes.

In contrast, with phosphinito-phosphinous acid Pd complexes the carbon-carbon triple bond inserts again into the Pd–C bond to form vinylidene species that after acidolysis furnish the [2+1] cycloaddition product. The formation of Pd-vinylidene species was supported by deuterium labelling experiments. It can be concluded that the phosphinito-phosphinous acid ligand is unique for this transformation because the two phosphorus atoms are inequivalent, but interchangeable. The asymmetric version of the reaction was explored with optically pure *P*-stereogenic SPOs and will be commented in the enantioselective catalysis section.

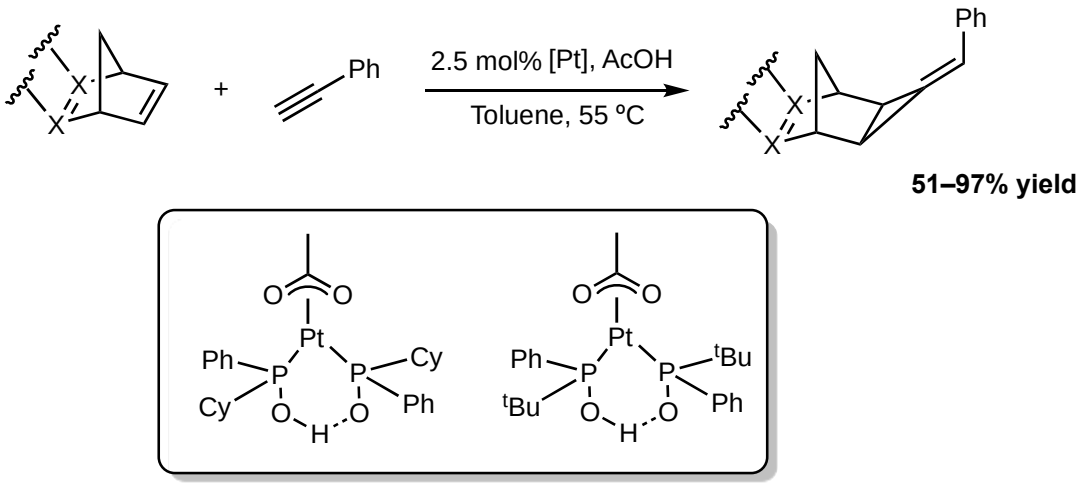
When the [2+1] cycloaddition reaction was attempted with propargyl acetates, it was found that these substrates triggered a tandem cycloaddition-ring expansion reaction giving various functionalised bicyclo[3.2.1]octadienes (Scheme 104).[168]



Scheme 104. [2+1]-cycloaddition/ring expansion tandem reaction.

This unusual reaction tandem reaction has been observed with several norbornadienes[168] and applied to the synthesis of seven-membered carbocycles.[259] It has to be noted that the reaction involves a vinylidenecyclopropane intermediate that can be generally isolated, which rearranges to the ring-expanded product.

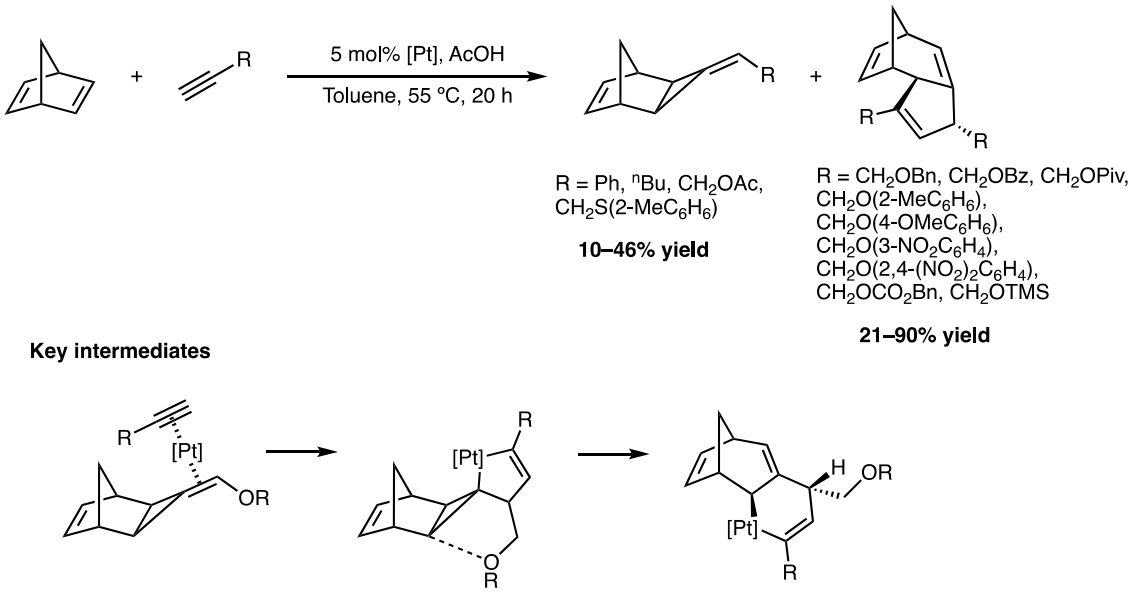
In parallel, the same group developed the Pt-catalysed version of the reaction of Scheme 102,[181] which constituted the first example of carbon-carbon bond formation catalysed by Pt-SPO species. The reactions proceed under mild conditions (55 ºC) and require the presence of acetic acid (Scheme 105).



Scheme 105. Selected examples of Pt-catalysed [2+1] cycloadditions.

It was found that in most cases Pt-based systems performed better than the Pd-based analogues. Like the Pd-catalysed reactions, Pt-vinylidene complexes were proposed as intermediates, but with important differences between the mechanisms for Pd- and Pt-catalysed reactions.[260]

When using propargyl acetates as substrates, a Pt-catalysed regio- and diastereoselective tandem [2+1]/[3+2] intermolecular cycloaddition reaction was developed (Scheme 106).[261]



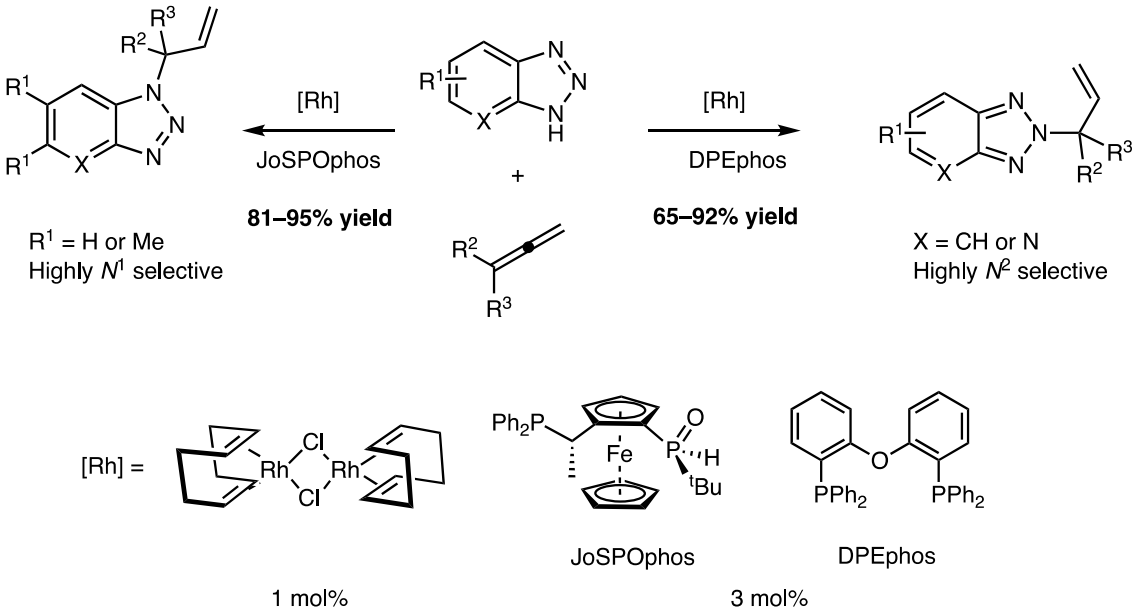
Scheme 106. Pt/SPO-catalysed tandem [2+1]/[3+2]-cycloaddition reactions.

This tandem reaction has a wide scope of substrates and allows the formation of tricyclic compounds in good yields and selectivities. The mechanism of the [3+2] cycloaddition[261] reaction is thought to involve platinacyclopentenes formed by oxidative

coupling between the alkyne and the methylenecyclopropane formed by the [2+1] cycloaddition.

5.10. Additions to allenes

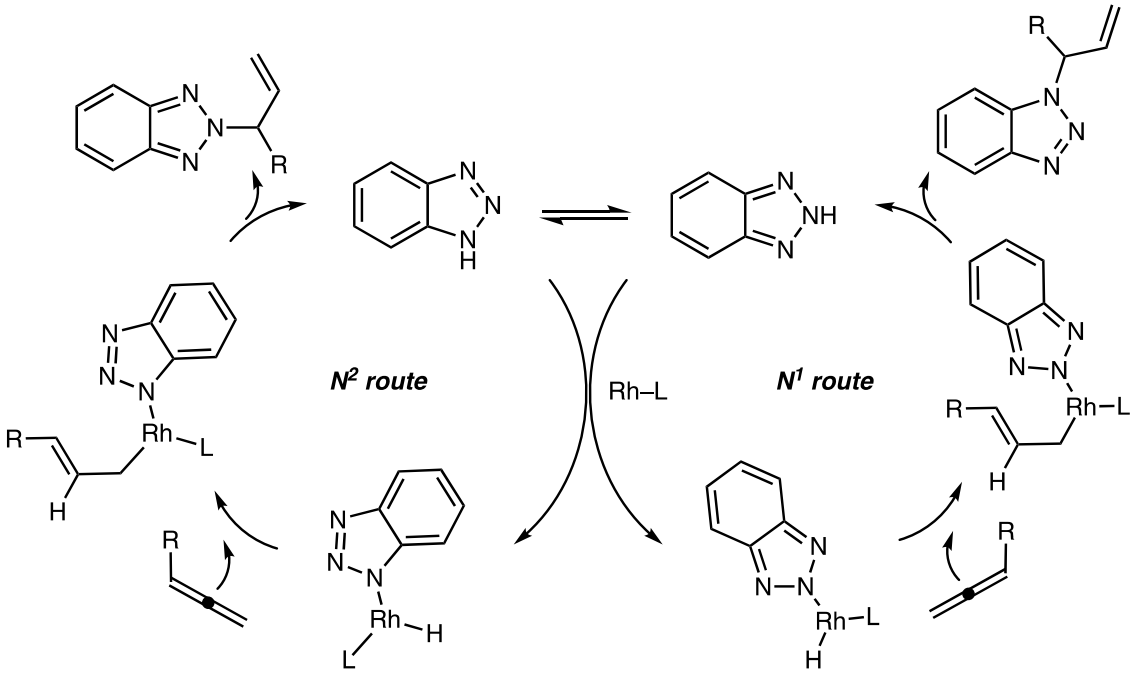
A few years ago Breit and coworkers[262] reported a Rh(I)-catalysed coupling of benzotriazoles with allenes, a C–N bond forming reaction. Due to the equilibrium between the N^1 and N^2 tautomers of 1,2,3-triazoles a mixture of N^1- and N^2-substituted products is usually found. An exceptionally high N^1-selectivity was found in the case of the SPO ligand named JoSPOphos in contrast to the high N^2-selectivity obtained with DPEphos (Scheme 107).



Scheme 107. Rh-catalysed coupling of benzotriazoles with allenes.

The catalytic system was robust and tolerated many modifications on the benzotriazole and the allene. Given that JoSPOphos is chiral, *P*-stereogenic SPO, some enantioinduction could be expected and indeed a 46% *ee* was observed.

The mechanism was studied by labelling experiments[262] and a plausible explanation for the formation of the two regioisomers could be found (Scheme 108).



Scheme 108. Mechanism for the Rh-catalysed coupling of benzotriazoles with allenes.

Further work from the same group expanded the Rh(I)/JoSPOphos catalysis to the coupling of allenes with pyrazoles[263] and tetrazoles,[264] the coupling of alkynes to triazoles[78] and to the hydroamination alkynes[265] but as these reactions gave very good enantioselectivities, they are described in the enantioselective catalysis section.

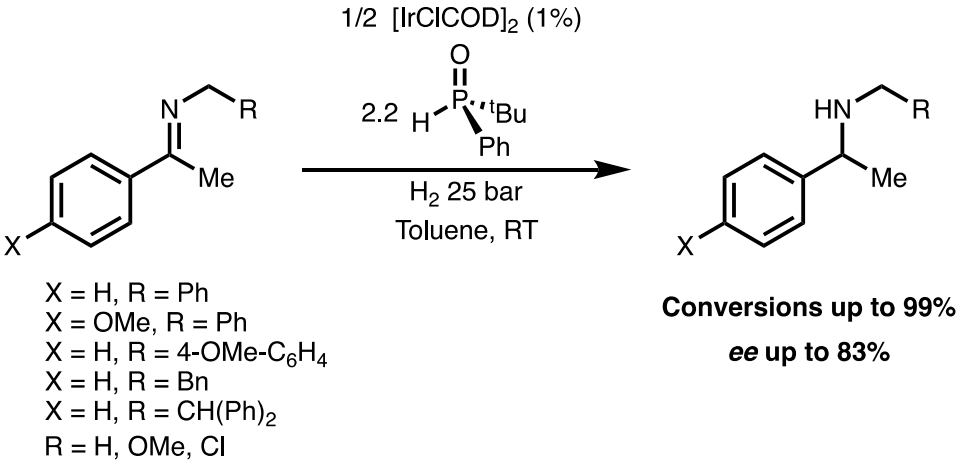
6. Enantioselective catalysis

Despite the fact that *P*-stereogenic SPOs are in general configurationally stable, they not have been profusely used in asymmetric catalysis and the same happens with the other types of chiral SPOs. The last years, however, have witnessed the appearance of very interesting results in asymmetric catalysis with SPOs, which bodes well for the future. Most of the best results in enantioselective catalysis with SPOs have been achieved with bidentate systems, although the most heavily studied chiral SPO is the *P*-stereogenic *tert*-butylphenylphosphine oxide.

6.1. Hydrogenation

The most thoroughly studied reaction in asymmetric homogeneous catalysis is by far hydrogenation. Unsurprisingly, several reports have described the use of SPOs in hydrogenation of several unsaturated substrates.

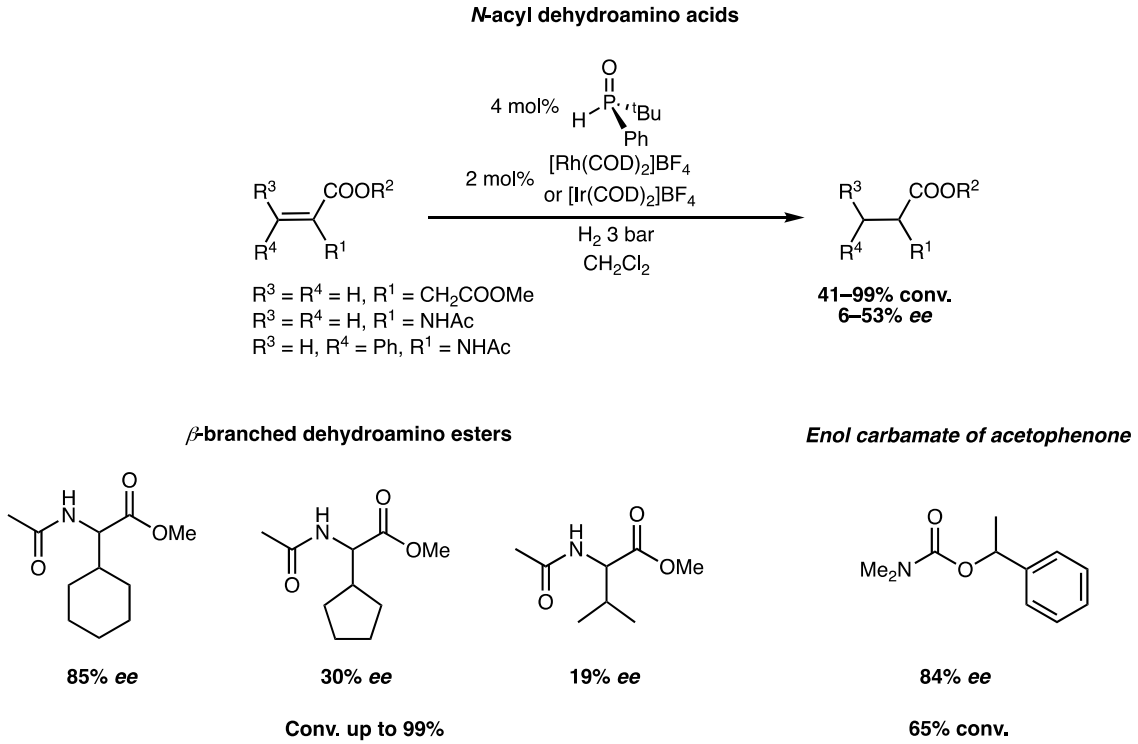
The first report on the use of an SPOs in asymmetric catalysis came from Minaard, Feringa, de Vries and coworkers,[66] who used several simple *P*-stereogenic SPOs (including *tert*-butylphenylphosphine oxide) obtained by preparative HPLC (Figure 3) in the Ir-catalysed hydrogenation of imines (Scheme 109).



Scheme 109. Asymmetric Ir/SPO-catalysed hydrogenation of imines.

With this system they were able to reduce several ketimines with relatively good conversions and selectivities.

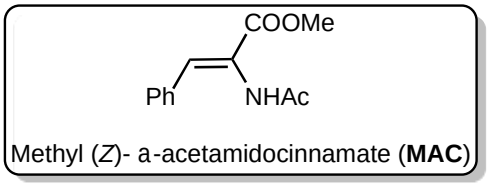
Immediately after this report, the same group applied the same ligands to the Rh-and Ir-catalysed reduction of functionalised alkenes[124] (Scheme 110).



Scheme 110. Asymmetric Rh- and Ir/SPO-catalysed hydrogenation of functionalised olefins.

It was found that the typical *tert*-butylphenylphosphine oxide was a versatile ligand in the Ir-catalysed hydrogenation of β-branched dehydroamino esters and in the Rh-catalysed hydrogenation of an enol carbamate. Interesting solvent effects on the absolute configuration of the hydrogenated product were found.

After these initial results, there was little activity in the field of hydrogenation with SPOs [38,67] because it became clear that in order to obtain better results competitive with the best ligands in asymmetric hydrogenation more elaborate systems were needed. In this line, in 2014 by Han and co-workers,[125] who described the *in situ* Rh-catalysed hydrogenation of α-acetamidocinnamates using optically pure *H*-menthylphosphinates, achieving enantioselectivities up to 99.6% with (R_P)-menthylbenzylphosphinate. They were able to grow suitable crystals for X-ray determination of a solution with $[Rh(COD)_2]OTf$ and the ligand ^{t}BuPhP(O)H and they found that the complexes formed did not contain the expected pseudobidentate bridge, but a OTf^- moiety instead (Figure 11).[125]



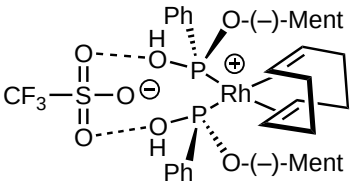
Methyl (*Z*)- a-acetamidocinnamate (**MAC**)

Feringa, de Vries

"*In situ*"

100% Conv., 31% *ee* (*S*)

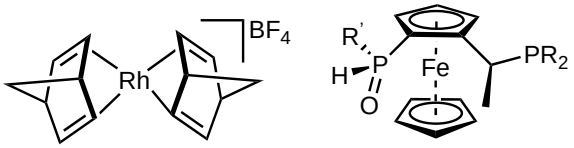
Han



100% Conv. 99.4% *ee*

Pfaltz

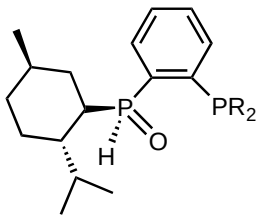
SPO–P ligands with chiral backbone



JoSPOphos

R = Ph, R' = ^{t}Bu, 97% *ee*
R = ^{t}Bu, R' = Ph, 90% *ee*
R = Ph, R' = Ph, 85% *ee*
R = ^{t}Bu, R' = ^{t}Bu, 99% *ee*

SPO–P ligands with chiral substituents



TerSPOphos

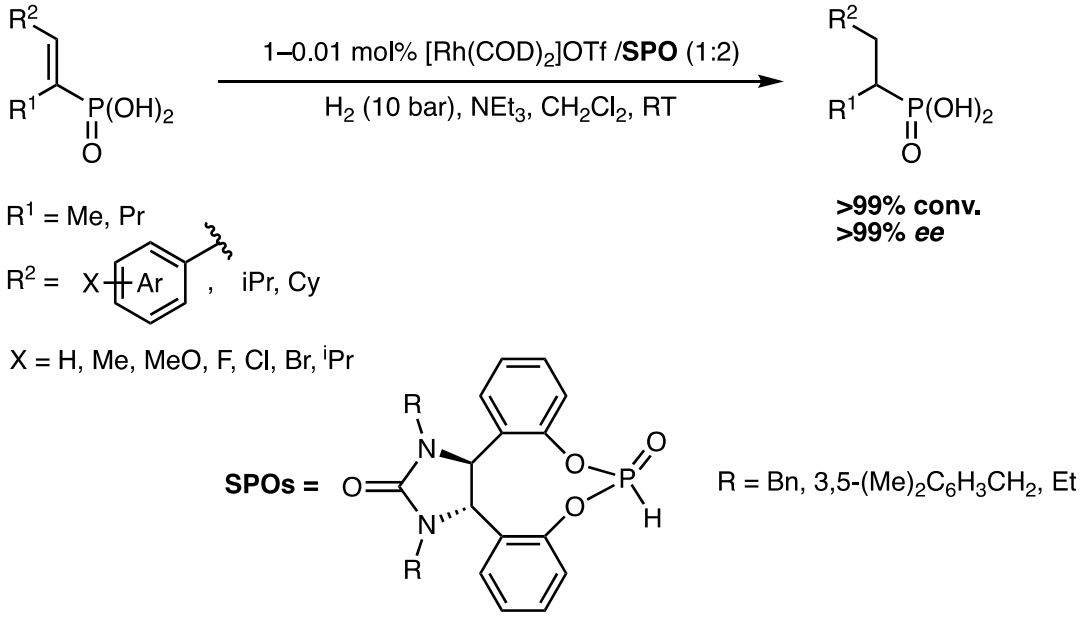
R = Ph, --- *ee*
R = 4-Tol, 96% *ee*
R = Cy, 94% *ee*

Figure 11. Rh(I)-catalysed asymmetric hydrogenation of MAC with chiral SPOs.

The best results in the field, however, were reported by Pfaltz and co-workers,[77] who considered that the scarce research done were due to the insufficient affinity of the SPO for Rh. With this in mind, they successfully combined an SPO with phosphino moiety, which should not only lead to a stronger coordination to the metal but also should give better-defined complexes. Indeed they successfully prepared two SPO–P ligands with chiral elements on the backbone as well as at the phosphorus atom of the SPO (Figure 11). The first SPO–P family (JoSPOphos, Scheme 19) was based on a chiral ferrocenyl backbone, which leads to ligands similar to the well-known Josiphos[266-268] while the second (TerSPOphos) contained a menthyl substituent. Both families were tested in the hydrogenation of α-acetamidocinnamates achieving the best results reported for these SPO systems, displaying enantioselectivities up to 99% *ee* and very high TOFs, of up to 20000 h^{-1}.

Pugin, Pfaltz and coworkers[77] also employed JoSPOphos in combination with [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] in the hydrogenation of β-ketoesters. They found that it was difficult to draw structure-selectivity relationships but managed to obtain a 92% *ee* in the hydrogenation of 2-oxopentanoate at very low catalyst loading under 1 bar of hydrogen. It was found that for these ligands the absolute configuration of the phosphorus atom controls the sense of the optical induction.

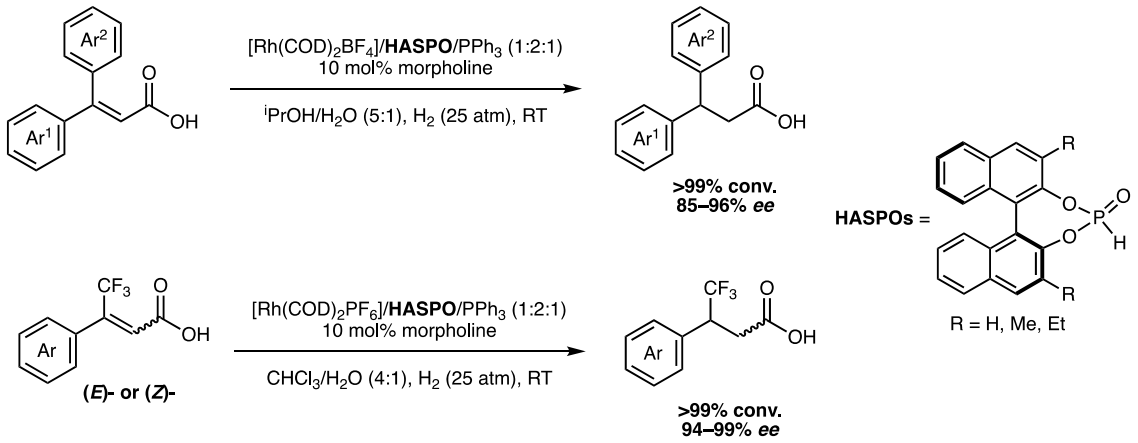
A couple of years later Ding and coworkers[269] was studying the Rh/phosphoramidite catalysed hydrogenation of α-substituted ethenylphosphonic acids and serendipitously discovered that the hydrolysis products[213] of certain phosphoramidites, which were HASPOs, were indeed excellent ligands for the reaction (Scheme 111).



Scheme 111. Rh/SPO-catalysed hydrogenation of ethenylphosphonic acids.

The evolved catalysts showed excellent enantioselectivity and catalytic activity in the asymmetric hydrogenation of many α-substituted ethenylphosphonic acids producing enantiopure phosphonic acids with biological interest. The authors hypothesised that the H-bonding interactions had a positive effect on catalysis (poor conversions were observed in protic solvents) and that two HASPOs produced a *pseudobidentate* ligand, as shown by X-ray crystallography.

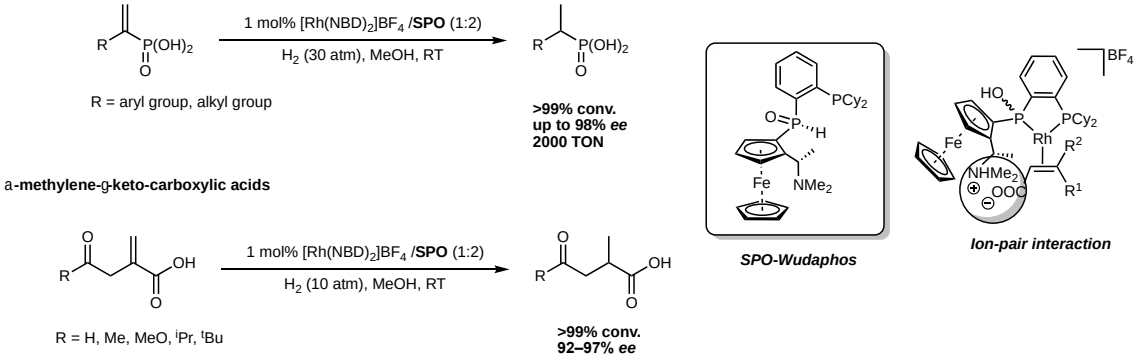
The same authors expanded this work to the preparation of bioactive building blocks by Rh(I)/HASPO-catalysed asymmetric hydrogenation of acrylic acids (Scheme 112).[270-272]



Scheme 112. Rh(I)/SPO/PPh_3-catalysed hydrogenation of acrylic acids.

Interestingly, they observed a synergistic effect[273] with sharp improvements on both activity and enantioselectivity when achiral triphenylphosphine and related ligands were employed along with the chiral HASPO ligand.

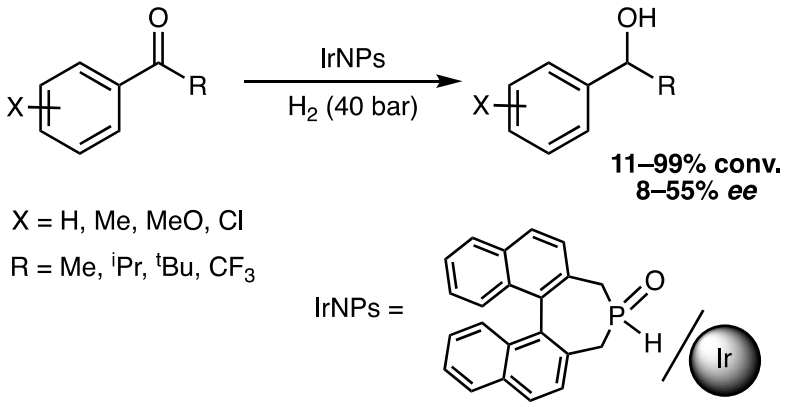
Recently, Dong, Zhang and coworkers[79,80,274] used their ferrocenyl-based ligands SPO-Wudaphos (Scheme 19) in the hydrogenation of α-methylene-γ-keto carboxylic acids,[80,275] and α-substituted ethenylphosphonic acids[274] obtaining exceedingly high enantioselectivities and very good conversions towards the hydrogenated product, which in many cases had biological applications (Scheme 113).



Scheme 113. Rh/Wudaphos-catalysed hydrogenations.

Both experimental and computational methods showed the important role of ion-pair and H-bond non-covalent interactions in the excellent performance of the ligands.

There is a report of van Leeuwen and coworkers[276] on the enantioselective hydrogenation of ketones by Ir-NPs stabilised by an atropoisomeric SPO (Scheme 68) that was unable to racemise under catalytic conditions (Scheme 114).



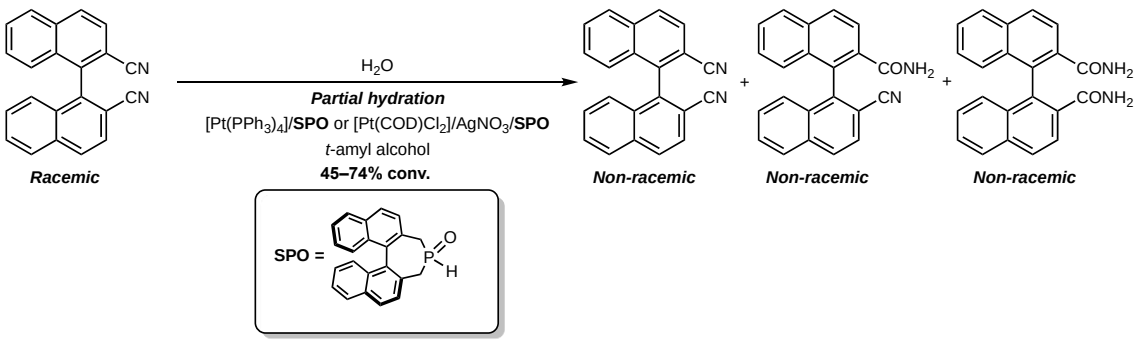
Scheme 114. Hydrogenation of ketones catalysed by Ir/SPO-stabilised NPs.

This study represented the first example of asymmetric hydrogenation on SPO-stabilised NPs and the first asymmetric hydrogenation catalysed by non-supported Ir-NPs. Although the enantioselectivities were modest, only one ligand was studied so there is ample room for improvement as more ligands are studied.

6.2. Nitrile hydration

One of the most important applications of SPOs in catalysis is in the hydration of nitriles, as it has been described in this review. The development of an asymmetric, version, however, is very rare. In 2004 Minnaard, Feringa and de Vries[277] attempted the kinetic resolution in the hydrolysis of racemic nitriles with Pt-catalysis using enantiopure ^{t}BuPhP(O)H but no resolution was found, possibly due to racemisation of the ligand during the reaction.

Much later, a report of van Leeuwen and coworkers,[180] working with the chiral Pt-SPO complexes of Scheme 68 in the hydration of aromatic nitriles (Scheme 90) offered more promising results. One of the substrates they studied was the axially chiral [1,1'-binaphthalene]-2,2'-dicarbonitrile. When this dinitrile (in racemic form) was mono- and dihydrated, a successful kinetic resolution was achieved (Scheme 115).

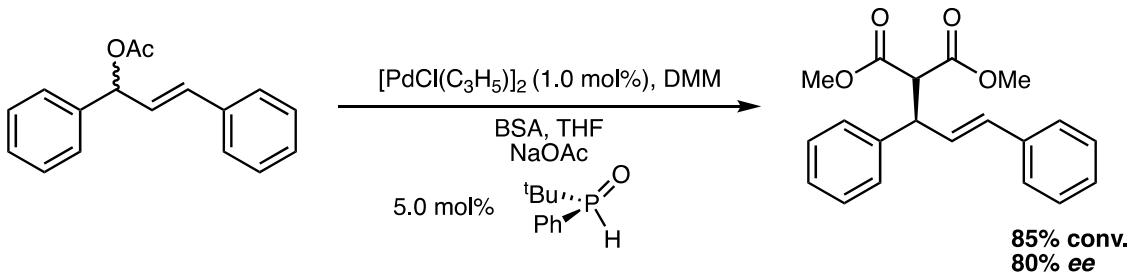


Scheme 115. Kinetic resolution of a racemic axially chiral dinitrile.

In this reaction the unconsumed dinitrile, the monocarboxamide and the biscarboxamide were formed in non-racemic form, especially for the latter, which could be obtained in very high enantioselectivity.

6.3. Allylic substitution

The enantioselective allylic substitution is a flagship reaction of asymmetric catalysis, especially with Pd-based catalysts. In spite of this, it has been scarcely explored with (strictly speaking) SPO ligands. To the best of our knowledge, only Dai and co-workers[86] studied the use of ^{t}BuPhP(O)H in the Pd-catalysed allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene, the model substrate, with dimethylmalonate (DMM) in the presence of bis(trimethylsilyl)acetamide (BSA) (Scheme 116).

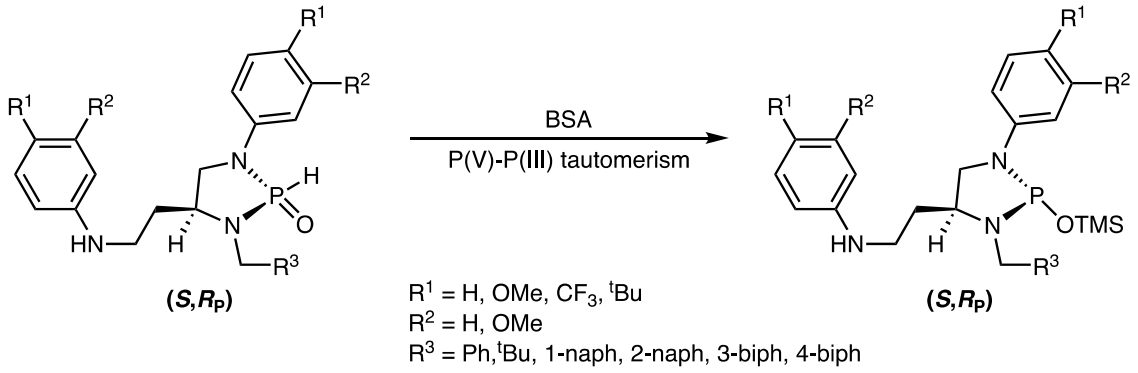


Scheme 116. Pd/SPO-catalysed asymmetric allylic alkylation of the model substrate.

The solvent, base, and other parameters of the reaction were varied and up to 80% *ee* were accomplished using an "*in situ*" generated palladium complex.

The situation is completely different when it comes to HASPO ligands because of a very successful family HASPOs developed by Hamada and coworkers in 2004,[46] the *P*-stereogenic DIAPHOX ligands (Scheme 11), afforded very good results in allylic substitution. For the model substrate (Scheme 116) they obtained[48] a 94% conversion and a 99% *ee* with the presence of BSA and zinc acetate. ^{31}P NMR studies

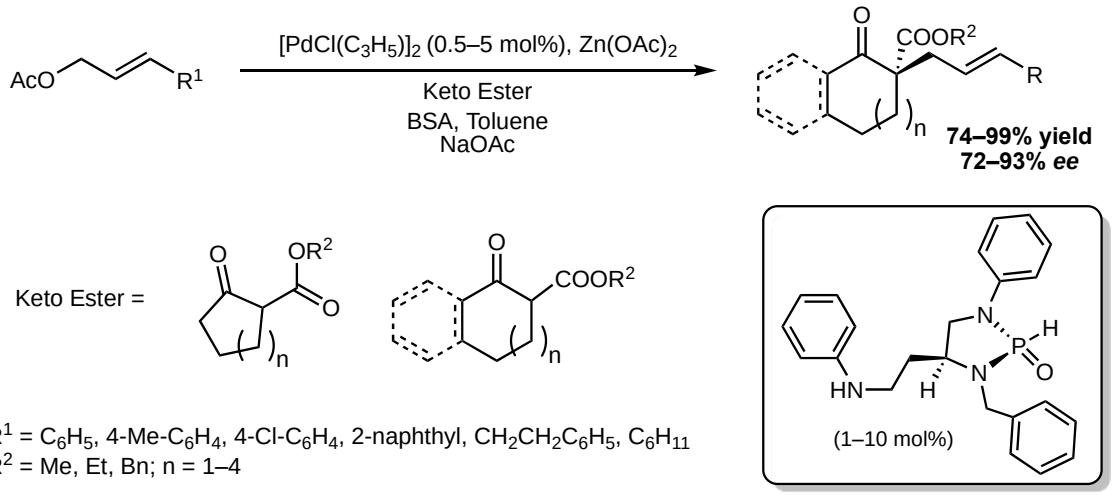
demonstrated that BSA triggered the tautomerisation of the DIAPHOX to the trivalent diamidophosphite (Scheme 117).



Scheme 117. DIAPHOX-HASPO ligands and their tautomerisation induced by BSA.

The results of some experiments showed that two molecules of DIAPHOX coordinated the Pd centre in a bis(monodentate) fashion and that the presence of zinc acetate was required in order to obtain good results. It was hypothesised that the exocyclic aminoethyl group has a directing effect upon the attacking nucleophile through an attractive secondary interaction.[47,48]

The most interesting result, however, was that the ligands were also very good in the formation of quaternary stereocentres[46] in high enantioselectivity (Scheme 118), an extremely important challenge, yet difficult, in organic synthesis.



Scheme 118. Asymmetric Pd/DIAPHOX-catalysed formation of quaternary stereocentres.

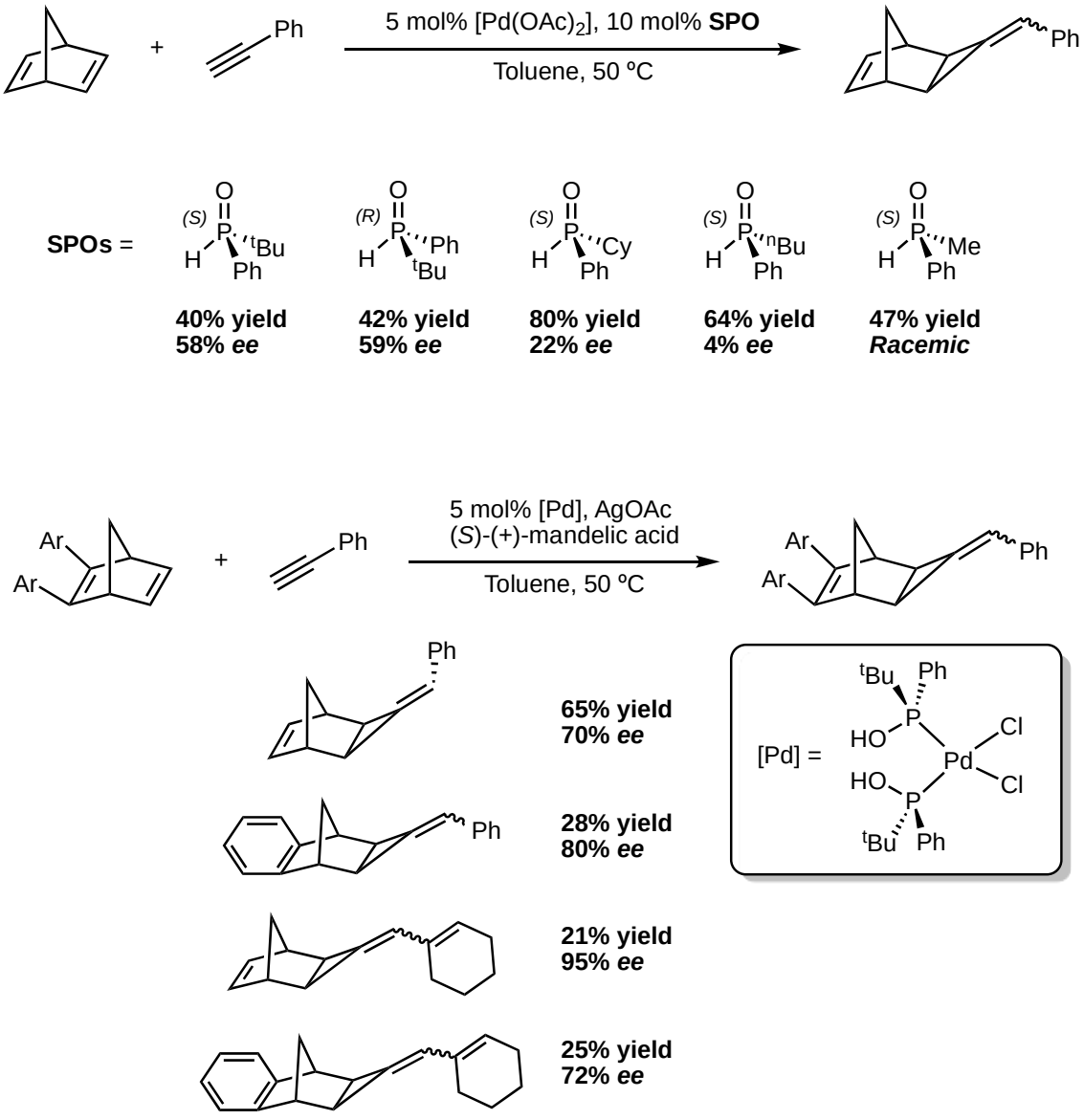
Given the promising results obtained with the DIAPHOX ligands, after the first report,[46] both the applicability and the study of the mechanism were studied in depth by Hamada and coworkers.[43,47,48,278-285] In addition, the reaction has been expanded to several types of Pd-catalysed allylic alkylations[43,282,283] aminations,[278,280,285] but also to

Ir-catalysed allylic alkylation[281] and amination.[279] These reactions have been applied to the formation of chiral centres in synthesis of biologically active products[285] and even to total syntheses.[284,286]

It should be noted that Nemoto and Hamada[10,45,49] have reviewed the application of the DIAPHOX ligands to allylic substitution and the reader is directed to these reviews to have the full account of their applicability.

6.4. Cycloadditions

The [2+1] cycloaddition products of Scheme 102 are chiral and display a particular chirality called geometrical enantiomorphic isomerism (also known as geometric isomerism or *cis-trans* isomerism) due to the *E* and *Z* configuration of the C–C double bond. Using optically pure *P*-stereogenic SPOs, Buono and coworkers[166,167,169] developed the asymmetric version of the Pd-catalysed [2+1] cycloaddition between norbornadienes and alkynes (Scheme 119).



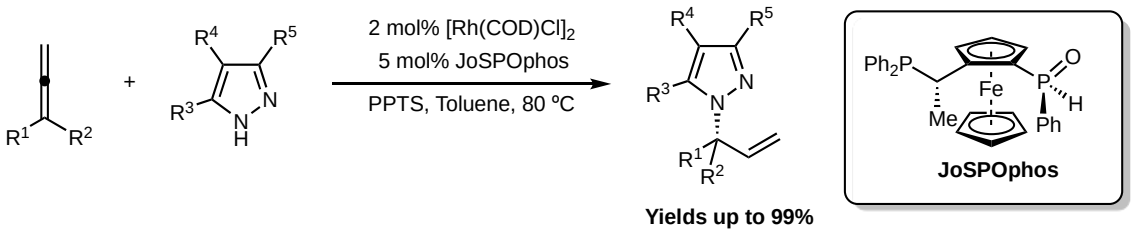
Scheme 119. Pd/SPO-catalysed asymmetric [2+1] between norbornadienes and alkynes.

Several simple chiral SPOs were employed but the most enantioselective was ^{t}BuPhP(O)H, with up to 59% *ee* for the reaction between norbornadiene and phenylacetylene.[167] An improvement of the enantioselectivity was possible by changing the reaction conditions and adding (*S*)-(+)-mandelic acid. With the optimised conditions, up to 95% *ee* could be obtained.[166]

6.5. Additions to allenes

In the Rh-catalysed addition of benzotriazoles to allenes, Breit and coworkers[262] reported a single result of 46% *ee* with the JoSPOphos ligand. Shortly after, the same group[263] reported the Rh(I)-catalysed asymmetric *N*-selective coupling of pyrazole

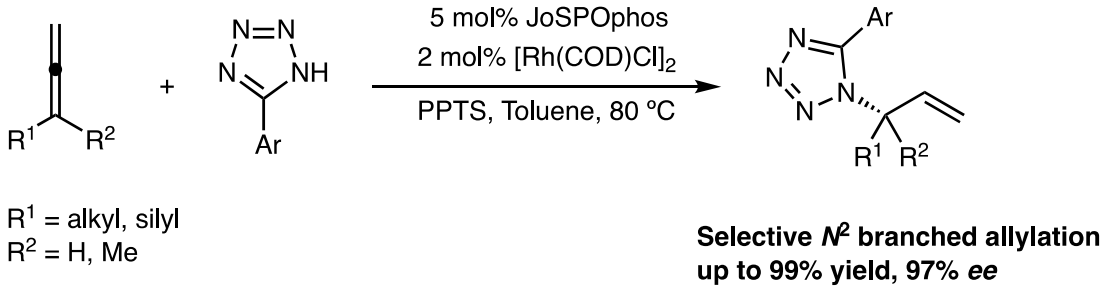
derivatives with terminal allenes to give secondary and tertiary allylic pyrazoles, which are important intermediates of medicinally important targets (Scheme 120).



Scheme 120. Rh(I)/JoSPOphos-catalysed asymmetric addition of pyrazoles to allenes.

The reaction was highly regio- and enantioselective with the ligand JoSPOphos and tolerated a broad range of substituted pyrazoles and allenes.

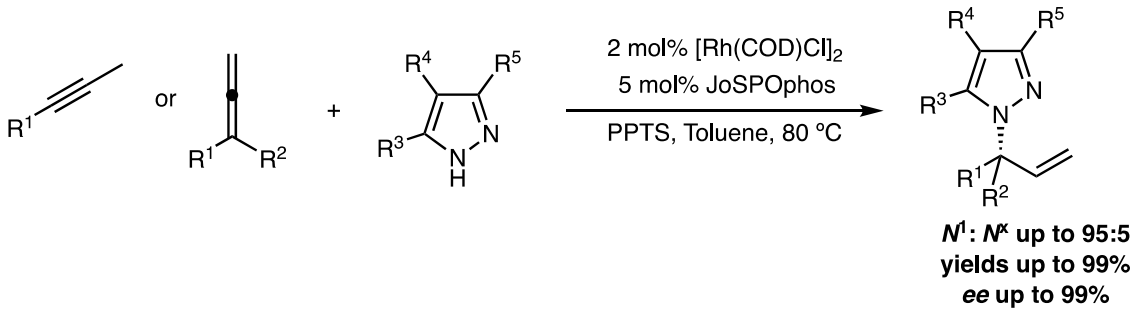
The same group expanded this chemistry to the asymmetric coupling of tetrazoles with allenes,[264] allowing the synthesis of tertiary and quaternary allylic C–N bonds in high enantioselectivity (Scheme 121).



Scheme 121. Rh(I)/JoSPOphos-catalysed asymmetric addition of tetrazoles to allenes.

Several typical bidentate phosphines such as DIOP and BINAP were used, but the best was JoSPOphos, reaching good yields for many substrates and enantioselectivities of up to 97% *ee*.

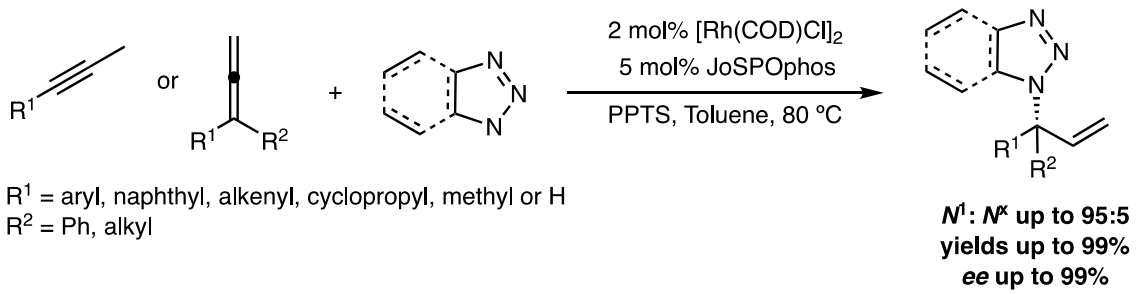
Further research from the same group[265] explored the enantioselective Rh-catalysed hydroamination of alkynes or allenes with pyrazoles (Scheme 122).



Scheme 122. Rh/JoSPOPhos-catalysed hydroamination of alkynes or allenes with pyrazoles.

This methodology allowed the functionalisation of both terminal and internal alkynes and also allenes with a broad range of pyrazoles. High chemo-, regio- and enantioselectivities were obtained towards the allylated pyrazoles, with remarkable functional group compatibility.

Quite recently, the same group[78] expanded their chemistry to the Rh-catalysed allylation of triazoles with alkynes or allenes (Scheme 123).

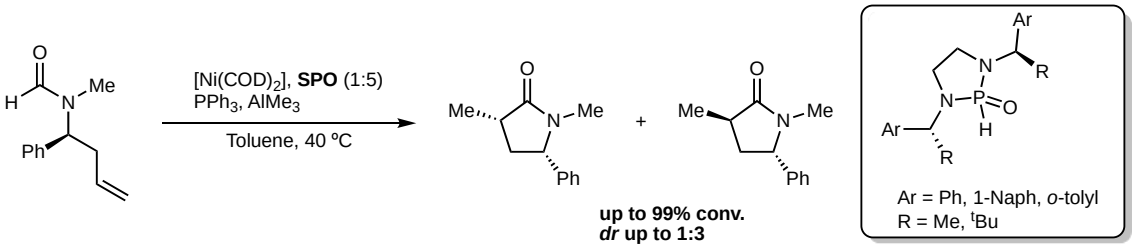


Scheme 123. Asymmetric Rh(I)-catalysed allylation of alkynes or allenes.

It was clear that the Rh/JoSPOphos system was very good at the regio- and enantioselective addition of triazoles to alkynes and terminal allenes. A broad substrate range of triazoles, alkynes and allenes provided *N*-allylated triazoles in very good yields and enantioselectivities. In this paper the synthesis of three new JoSPOphos ligands is described.

6.6. Hydrocarbamoylation

Donets and Cramer[287] reported Ni/Al-catalysed intramolecular hydrocarbamoylation of allylic formamides with a diaminophosphine oxide HASPO (Scheme 124).



Scheme 124. Asymmetric hydrocarbamoylation of allylic formamides.

The bulky HASPO, inspired by the work of Hamada and coworkers with DIAPHOX (see the allylic substitution part) was readily accessible and is believed to simultaneously bond to the Ni centre and the aluminium Lewis acid. This bimetallic catalyst required the presence of a monodentate phosphine to displace the cyclooctadiene. With this

system, excellent results in the asymmetric catalytic synthesis of chiral γ-lactams were obtained by C–H activation of formamides.

7. Conclusions

This review, although not in a fully comprehensive way aims to give a good grasp of the amazing variety of architectures that SPO ligands create when they coordinate to transition metals and they modularity and variety of roles that play in catalysis. Indeed, usually the introductions of the papers exploring the catalytic applications of SPOs in catalysis highlight the air-stability of SPOs in contrast to classic phosphines. After analysing the literature on SPOs over the last 50 years it is clear that SPOs are much more than "air-stable versions of phosphines" but they have their own idiosyncrasy and hold an immense potential in catalysis. In addition some SPOs have given impressive catalytic results including in asymmetric catalysis.

Despite all this, the truth is that SPOs still remain infrequently used in catalysis. This can be attributed to several factors. The first is that there is a lack of synthetic methods for SPOs. The most common synthesis is still the classic hydrolysis of chlorophosphines, an efficient method but only for the simplest SPOs, whose chlorophosphine precursors are commercially available. The scarcity of efficient synthetic methods is especially true for chiral SPOs and to make things worse, the case of *P*-stereogenic SPOs the hydrolysis method cannot be used since enantiopure chlorophosphines are very difficult to obtain. The good news is that the wealth of new synthetic phosphorus chemistry appearing in the recent years is also impacting the preparation of SPOs, especially the chiral ones and hence exciting new SPOs can be expected. Another factor that hampers a more widespread use of SPOs in catalysis is that the stereoelectronic properties of SPOs are still poorly understood, especially compared to phosphines and carbenes and the same can be said about the mechanism of metal-assisted tautomerisations. In addition, the coordination chemistry of SPOs is complicated and frequently changes in the course of a catalytic reaction. At present, the detailed factors that determine the coordination mode of SPOs remain speculative at best. Needless to say, a much better knowledge of all these aspects is required to understand the exact role of a SPO in catalysis. Fortunately, our knowledge is continuously improving not only with experimental results but also with increasingly insightful theoretical studies, usually employing DFT-based methods. We are confident, therefore, that when the synthetic and mechanistic challenges associated with SPOs are met, many new accomplishments will be seen in the use of SPOs in catalysis.

8. Acknowledgements

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