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Late Stage Modific ations of P-Containing Ligands using Transition-Metal-Catalysed C–H Bond Functionalisation

Zhuan Zhang[a], Pierre H. Dixneuf[a] * and Jean-François Soulé[a] *

Phosphorus containing molecules have seen widespread applications for the development of innovative metal ligand catalysts and materials. In recent years, the implentation of late-stage modifications of phosphorus derivatives *via ortho*-regioselective C–H bond functionnalisations have led to invent faster and better ways for the synthesis of complex ligands by creating new reactions with low impact on the environement. This Feature article highlights transition-metal catalysed regioselective C–H bond functionalisations of phosphorus-containing molecules, in which the phosphorus containing unit play the role of the directing group for the C–H bond activation and the syntheses of new functional phosphorus derivatives.

Introduction

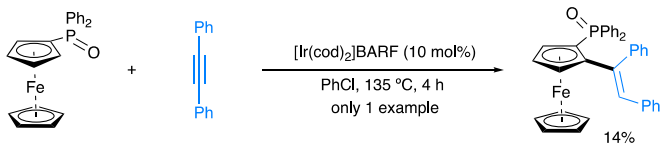
During the last decade efficient metal-catalysed activations of C–H bonds, followed by their selective functionalisations, have tremendously contributed to improve the synthetic methods of complex molecules and molecular materials with respect to classical catalytic cross coupling reactions, as they offer cleaner processes and much better atom economy.[1] The efficiency of catalytic C–H bond activation/functionalisation is now allowing late-stage diversification of functional molecules[2] and direct further functionalisation of metal catalysts, photocatalysts or molecular materials for optical properties.[3]

Organophosphorus compounds, of which their oxidation state can be easily modified, constitute an important class of molecules for their numerous applications in medicinal,[4] synthesis,[5] materials,[6] organocatalysts,[7] and especially as crucial ligand in metal-phosphine catalysts,[8] including the chiral ones.[9] Consequently, the application of the late stage functionalisations to phosphorous derivative C–H bonds constitutes a great challenge. The use of phosphines as directing groups for direct functionalisation of their aryl *ortho* C–H bonds has been rarely achieved as the P(III)-metal bonds in catalysts are usually too strong to be dissociated after functionalisation. In addition, the *ortho* C–H bond activation of aryl-phosphine-metal complexes is expected to lead to a difficult to reach 4-membered metallocycle intermediate. By contrast, phosphine oxides or sulphides, resulting from easy oxidation of phosphines, have been used as weakly coordinating directing groups for efficient C–H bond activation and functionalisation, *via* 5- or 6-membered metallacycle intermediates. Thus, they constitute excellent starting substrates for the late-stage functionalisation of their C–H bonds to afford after reduction new functional phosphines.

Illustrating recent studies in the field, including some of our own work, this feature article highlights the potential of C–H bond activations/functionalisations, in which a phosphorus containing moiety acts as a directing group, for the preparation of new functional phosphines. It is organized depending on the nature of the involved reactions: successively hydroarylation, alkenylation, alkylation, arylation, amination, C–O bonds formation, cyanation and borylation will be presented. Intramolecular C–H bond functionalisations leading to polycyclic phosphorous containing derivatives will not be retained in this review.[10] In addition, annulation reactions of phosphine oxides and sulphides,[11] which usually involve the formal insertion of alkyne or alkene into both *ortho*-aryl C–H and heteroatom-hydrogen bonds, will not be discussed here.

1. Hydroarylation *of* alkynes using phosphine oxides derivatives

In 2012, during their investigations on iridium-catalysed C–H bond alkenylation and alkylation of ferrocenes bearing different directing groups (e.g., 2-pyridine or imines), Shibata and co-workers reported the first example of the use of phosphine oxide as directing group for C–H bond activation/functionalisation (Scheme 1).[12] The C–H bond alkenylation of ferrocene derivatives was performed using 10 mol% $[Ir(cod)_2]$BARF [BARF = tetrakis(3,5-trifluoromethylphenyl)borate] with 2 equivalents of diphenylacetylene in chlorobenzene at 135 ºC. Diphenylphosphine oxide is used as a directing group to form planar chiral ferrocenyl phosphine oxide, albeit in a low yield. But it is shown that C–H bonds on the ferrocene unit are more reactive that those of the phenyl group.



Scheme 1. Ir-catalysed *ortho*-alkenylation of ferrocenylphosphine oxide

In 2013, Glorius and co-workers reported the *ortho*-alkenylation of aryl phosphonates and phosphonamides (Scheme 2).[10c] $[Cp^*RhCl_2]_2$ with $AgSbF_6$ in combination with 10 mol % $Cu(OAc)_2$ and 1.0 equiv PivOH as an additive at 110 ºC exhibited good catalytic activity with high stereoselectivity for the *E*- alkenylation of aryl phosphonamides; whereas, the aryl phosphonates are alkenylated in a poor E/Z ratio.

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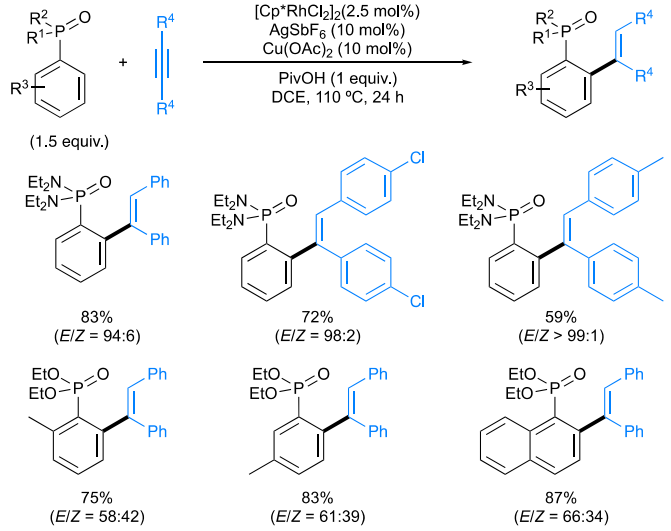
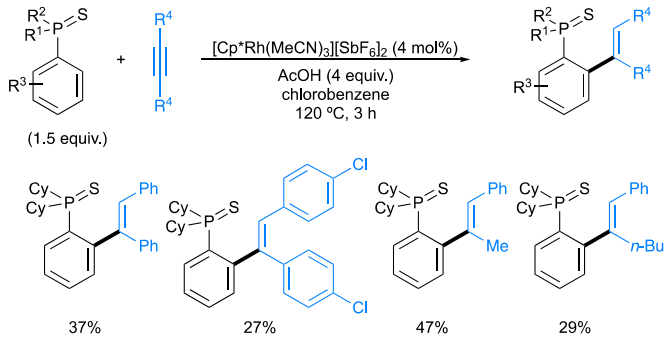


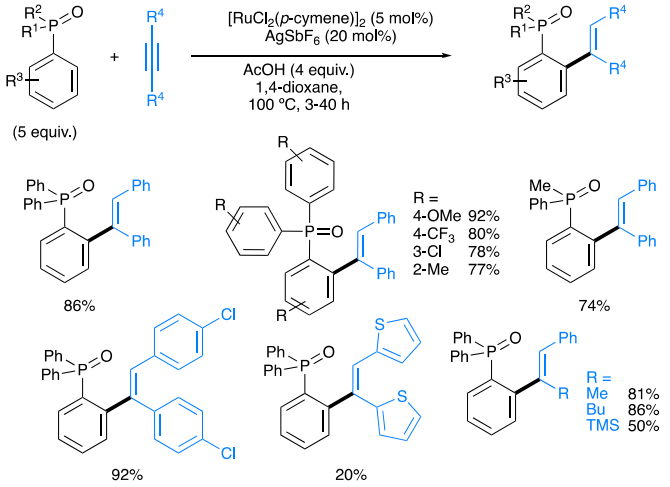
Scheme 2. Rh(III)-catalysed *ortho*-alkenylation of aryl phosphonates and phosphonamides with alkynes

In 2014, Satoh, Miura and co-workers demonstrated that phenylphosphine sulphides can also undergo proximal catalytic alkenylation with alkynes using Cp*Rh(III) under redox-neutral conditions but with acetic acid as proton source.[13] The reaction involves C–H bond cleavage directed by the P=S group to produce *ortho*-alkenylated phenylphosphine sulphides in moderate yields (Scheme 3).[13]



Scheme 3. Rh-catalysed *ortho*-alkenylation of phenylphosphine sulphides with alkynes

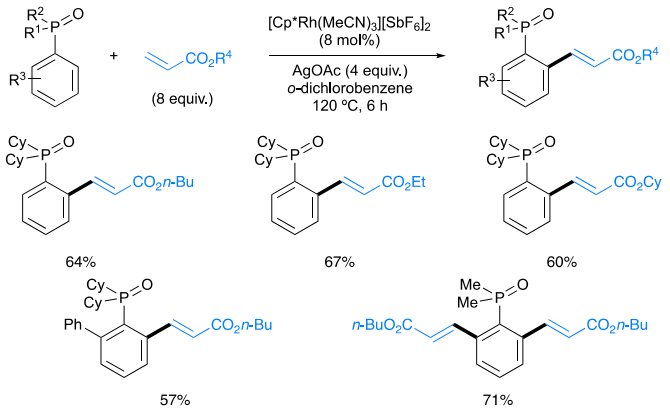
It is now also possible to perform the alkyne insertion into C–H bonds using phosphine oxide as formal directing group with ruthenium(II) catalysis (Scheme 4).[14] Tri-, di-, and monoarylphosphine oxides are alkenylated using $[RuCl_2(p\text{-cymene})]_2$ catalyst in concert with $AgSbF_6$ as chloro abstractor in the presence of acetic acid. The reaction tolerates a wide range of substituents on both arylphosphine oxides and internal alkynes. It is important to note that when unsymmetrical alkyne was used the reaction is completely stereo- and regioselective. The authors proposed a reaction pathway involving *ortho*-metallation –in which P=O acts as directing– followed by alkyne insertion into the 5 membered metallacycle and then in the presence of AcOH the protonolysis of Ru–C bond occurred with the regeneration of Ru(II) catalyst (see Figure 1).



Scheme 4. Ru-catalysed *ortho*-alkenylation of arylphosphine oxides with alkynes

2. Alkenylation of arylphosphine oxides with alkenes

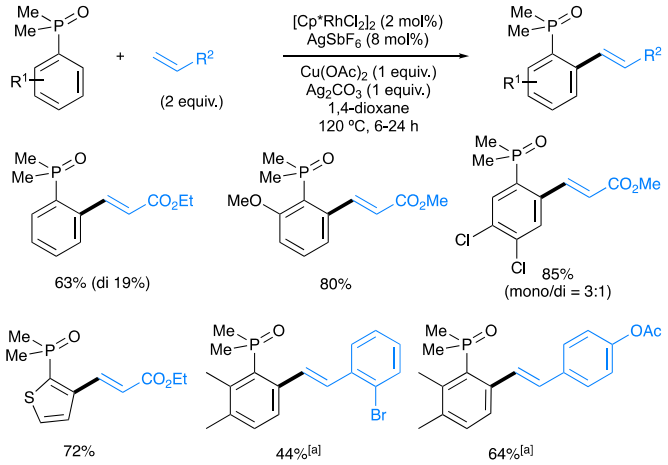
In 2013, Satoh, Miura and co-workers described the *ortho*-alkenylation of arylphosphine oxides with activated alkenes (Scheme 5).[15] In the presence of large excess of acrylates, mono arylphosphine oxides are *ortho*-alkenylated in moderate yields using $[Cp^*Rh(MeCN)_3][SbF_6]_2$/4AgOAc as catalytic system at 120 ºC. Interestingly, they succeeded in the late-stage modification of Cy-JohnPhos oxide (dicyclohexyl(biphenyl-2-yl)-phosphine oxide) allowing the formation of *ortho*-alkylated product in 57% yield. In the case of sterically less hindered dimethyl(phenyl)phosphine oxide, the authors observed the dialkenylation. It is important to note that in this reaction the silver salt seem to act as an oxidant.



Scheme 5. Rh-catalysed *ortho*-alkenylation of arylphosphine oxides with alkenes

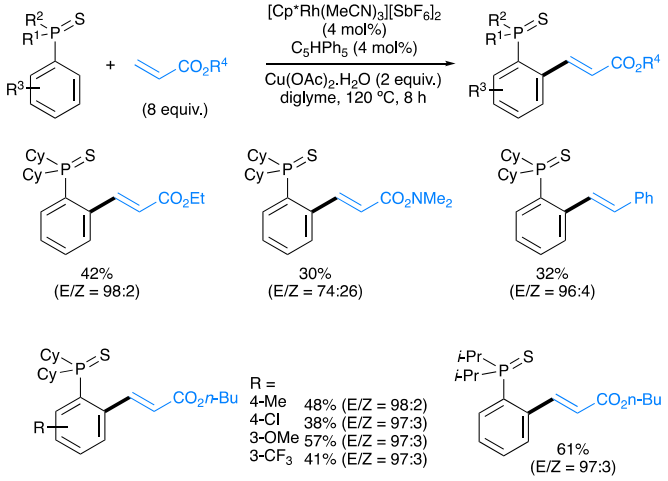
As demonstrated by Lee and co-workers, it is now possible to achieve the mono-alkenylation at *ortho*-position of P=O of dimethyl(phenyl)phosphine oxide with acrylate in 63% yield using $[Cp^*RhCl_2]_2$ / 4 $AgSbF_6$ in combination with 1 equivalent of $Cu(OAc)_2$ and 1.0 equivalent Ag_2CO_3 as an oxidant and base (Scheme 6).[16] However, again 19% of dialkenylation product was produced. They generalized the reaction to substituted dimethyl(phenyl)phosphine oxides in better yields. The reaction is also operative with styrene derivatives, provided

that the reaction is conducted in absence of $Cu(OAc)_2$ and in THF.



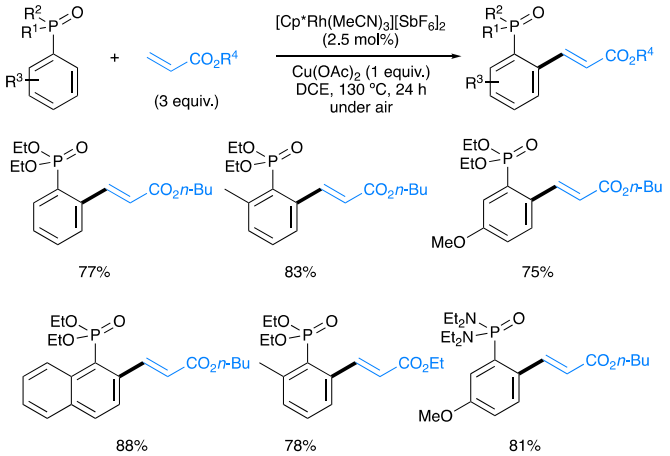
Scheme 6. Rh-catalysed mono *ortho*-alkenylation of dimethyl(phenyl)phosphine oxide with alkenes [a] Reaction performed in absence of $Cu(OAc)_2$ in THF insetad of 1,4-dioxane.

Phenylphosphine sulphides were also employed by Satoh, Miura and co-workers in Cp*Rh(III)-catalysed *ortho*-alkenylation with activated alkenes (Scheme 7). The optimized reaction conditions are found using $[Cp^*Rh(MeCN)_3][SbF_6]_2$ as catalyst in the presence of $Cu(OAc)_2$ as oxidant and base in diglyme at 120 ºC. The authors found that the addition of 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (C_5HPh_5) slightly improved the yield into the desired functionalized phenylphosphine sulphides, although its exact role is not clear. The *ortho*-alkenylated phenylphosphine sulphides are obtained in moderate yields with contamination by trace amounts of the *Z*-isomers. The authors did not observe a major effect of the substituent on the phenyl group. However, they did not demonstrate if the reaction with di- or tri-arylphosphine sulphides as substrates is also operative.



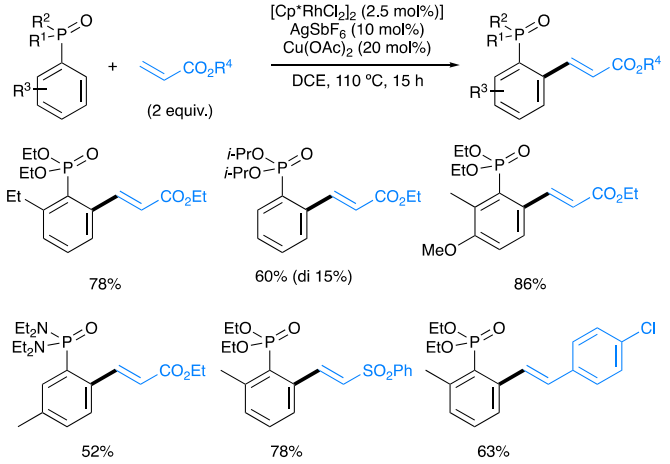
Scheme 7. Rh-catalysed *ortho*-alkenylation of phenylphosphine sulphides with alkenes. *E/Z* ratio determined by ^{1}H NMR.

In 2013, Glorious and co-workers also reported the C–H bond alkenylation of aryl phosphonates with acrylates in good yields using the pregenerated cationic rhodium species $[Cp^*Rh(MeCN)_3][SbF_6]_2$ in the presence of stoichiometric amount of $Cu(OAc)_2$ as oxidant in DCE under air (Scheme 8).[10c] The reaction is not sensitive to the electronic and steric factors on the aryl group of phosphonates. This *ortho*-functionalisation can also be performed with aryl phosphonamides.



Scheme 8. Rh(III)-catalysed *ortho*-alkenylation of aryl phosphonates and phosphonamides with acrylate

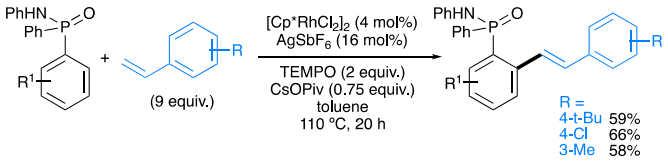
At the same time, Kim and co-workers reported the similar Rh(III)-catalysed *ortho*-alkenylation of aryl phosphonates and phosphonamides (Scheme 9).[17] The reaction conditions are analogous, albeit they employed only catalytic amount of $Cu(OAc)_2$ under air. While it is not mentioned by the authors, we believe that the trace of oxygen plays the role of the terminal oxidant for such oxidative couplings. The reaction is not limited to acrylates as vinyl sulfone and styrenes have been also successfully coupled with aryl phosphonates.



Scheme 9. Rh(III)-catalysed *ortho*-alkenylation of aryl phosphonates and phosphonamides with acrylate.

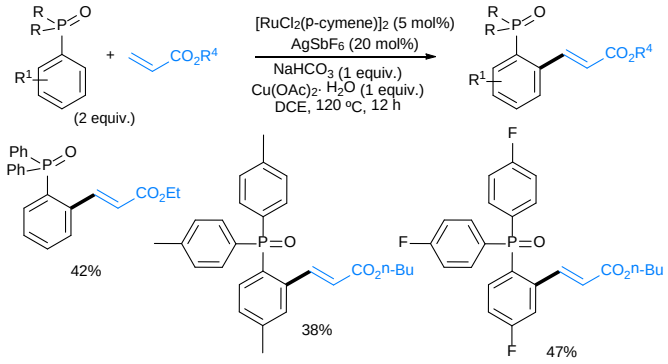
During their investigation on annulation reaction between phosphonamide and activated alkenes or alkynes, Lee and co-workers also demonstrated that phosphonamide can act as a directing group in Rh(III)-catalysed *ortho*-alkenylation with styrenes even in the presence of TEMPO (Scheme 10).[18] The

reaction was found to be sluggish with non–activated alkenes and only mono-alkenylation occurred even in the presence of access amount of styrene derivatives.



Scheme 10. Rh(III)-catalysed *ortho*-alkenylation of aryl phosphonamide with alkenes

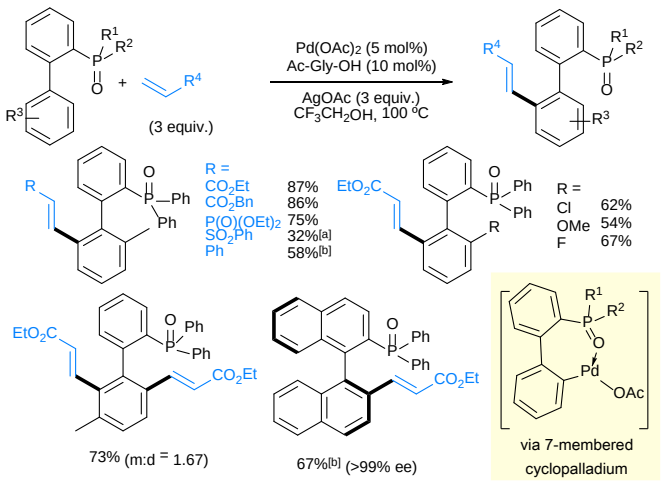
In 2017, our group reported the first example of *ortho*-alkenylation with alkenes of triarylphosphine oxides using Ru(II) catalyst (Scheme 11).[19] We employed $[RuCl_2(p\text{-cymene})]_2$ in the presence of $NaHCO_3$ as base and $Cu(OAc)_2$ as oxidant in dichloroethane at 120 ºC. Diversely substituted triarylphosphine oxides are mono-alkylated at *ortho*-position in moderate yields with acrylates. An excess amount of triarylphosphine oxides is required to prevent di or tri-alkenylation side-reaction. *Completed alkenylation or alkylation can now be controlled.*[19] As shown in the Figure 1, we explained the key role of the reaction pH and oxidant on the selectivity of the reaction, namely, alkenylation under basic media versus alkylation in acidic conditions (Scheme 18).



Scheme 11. Ru(II)- catalysed *ortho*-alkenylation of triaryl phosphine oxides with alkenes

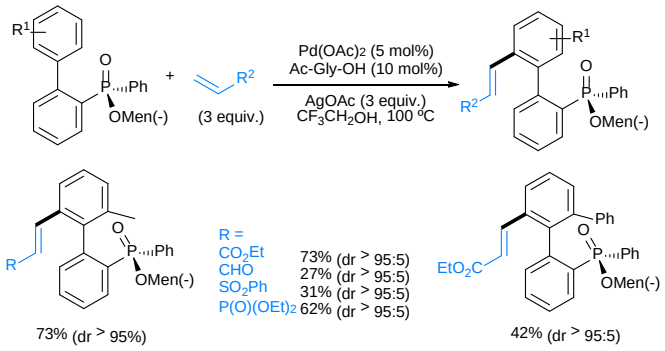
Palladium catalysts are also able to achieve C–H bond alkenylation for the synthesis of phosphine–alkene ligands. In 2013, Yang and co-workers disclosed that biphenylphosphine oxides, such as MePhos oxide, underwent C–H bond alkenylation at *ortho*' position using 5 mol% $Pd(OAc)_2$ in concert with 10 mol% of amino acid (L-Ac-Gly-OH) as ligand in the presence of AgOAc as base/oxidant in trifluoroethanol (Scheme 12).[20] Activated alkenes such as acrylate or vinylsulfone displayed high reactivities, while with styrene double amount of catalyst loading is required. A wide variety of substituents on the biphenylphosphine oxides are tolerated but when there is no substituent at the *ortho*' position dialkenylation reaction occurred. Under these conditions, triphenylphosphine oxide is not reactive.

It is noteworthy that the authors also showed that using commercial chiral binaphthyl-based diphenylphosphine oxide as the substrate, they are able to synthesize different chiral alkene–phosphine hybrid oxide compounds without epimerization. The authors reasonably postulate that thus reaction involved 7-membered cyclopalladium intermediate.



Scheme 12. Pd-Catalysed alkenylation of biphenylphosphine oxides. [a] Using 10 mol% of $Pd(OAc)_2$. [b] Using 10 mol% of $Pd(OAc)_2$, 20 mol% of Ac-Gly-OH and 5 equiv. of AgOAc.

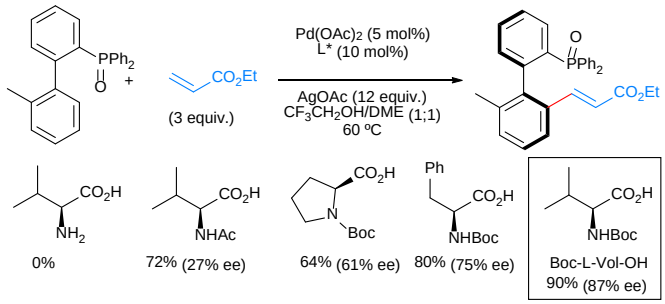
The same group has synthetized chiral biaryl phosphates using Pd(II)-catalysed asymmetric *ortho'*-direct alkenylation through dynamic kinetic resolution (Scheme 13).[21] From axially racemic biphenylphosphine oxides, bearing enantiopure menthyl phenylphosphate group as directing group, similar reaction conditions, excepted the presence of $Cu(OAc)_2$ as oxidant, allowed the formation of alkenylated products containing both axially chirality and the previous P stereogenic center. A wide substrate scope is demonstrated and the reaction occurred in all cases with a good diastereomeric ratio (dr>95:5).



Scheme 13. Pd-Catalysed asymmetric alkenylation of biphenylphosphine oxides

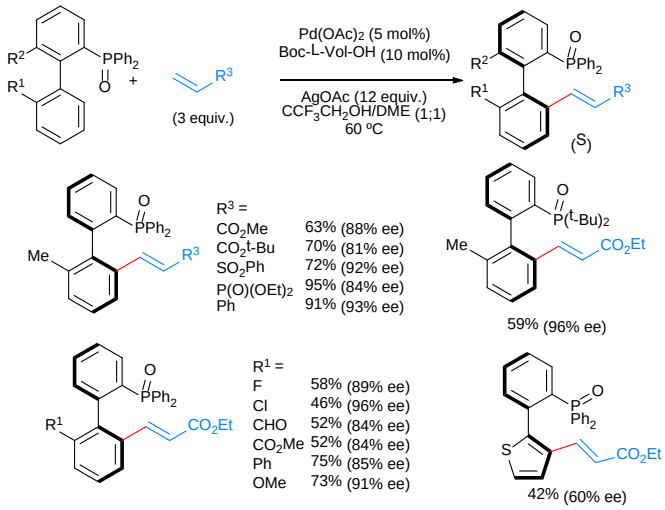
In 2017, Yang and co-workers succeeded in the synthesis of atropoisomeric phosphine–olefin ligand *via* the enantioselective C–H olefination of biphenylphosphine oxides.[22] From (2'-methyl-[1,1'-biphenyl]-2-yl)diphenylphosphine oxide and ethyl acrylate in the presence of 5 mol% $Pd(OAc)_2$ and 3 equivalents of AgOAc, (protected)amino acids are evaluated toward enantioselective C–H alkenylation (Scheme 14). They demonstrated that the unprotected amino acids such as L-Val-OH inhibited the

reaction, whereas monoprotected amino acids such as Ac-L-Val-OH, Boc-L-Pro-OH, Boc-L-Phe-OH, and others allowed the formation of phosphine oxide–olefin ligand in good yield with moderate ee. The best result is obtained using Boc-L-Val-OH as the ligand and the corresponding chiral biaryl phosphine–olefin hybrid ligands is isolated in 90% yield with 87% *ee*.



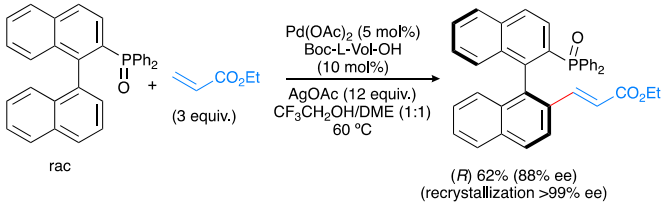
Scheme 14. Ligand effect on Pd-Catalysed enantioselective alkenylation of MePhos oxides

Yang et al. have also shown that various electron-deficient olefins such as butyl, benzyl, phosphite, and sulfonyl acrylates are compatible with this enantioselective direct C–H alkenylation reaction allowing the formation of corresponding products in good yields with 84%– 92% *ee* values. Styrene derivatives also led to (*S*)-alkenylated products in moderate-to-good yields with high *ee* values A bulky P(O)(t-Bu)$_2$ group allows better stereoselectivity (96% ee). An electron-withdrawing substituent at *ortho'*-position of the biphenylphosphine oxide gave lower yield without affecting the *ee* value, whereas electron-donating group improved the yield (Scheme 15).[22] The authors have confirmed the absolute configuration of the (*S*) products by single-crystal X-ray crystallography, which also explains why the transition state of the (*S*)-Pd complex is more favourable than the (*R*)-Pd complex in the C–H activation step.



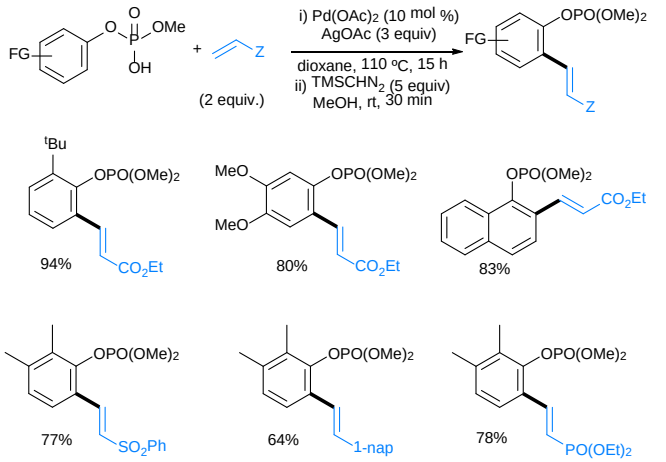
Scheme 15. Pd-Catalysed enantioselective alkenylation of biphenylphosphine oxides

They have also used the racemic binaphthyl diphenyl oxide as a substrate to examine this enantioselective C–H alkenylation reaction and they obtained (*S*) phosphine–olefin ligand in 62% yield with 88% *ee*, which could be improved to 99% *ee* by simple recrystallisation (Scheme 16).[22]



Scheme 16. Pd-Catalysed enantioselective alkenylation of racemic binaphthyl diphenyl oxide

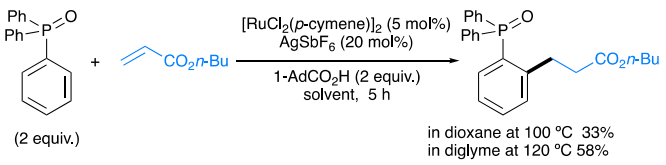
In 2013 Kim and Lee[23] reported the ortho alkenylation of aryl group directed this time by a mono-phosphoric acid group (Scheme 17).[23] The alkenylation was performed efficiently using a variety of electrophilic or aryl alkenes with the Pd(OAc)$_2$/AgOAc catalyst. The success was due to the easy formation of a 6-membered metallacycle intermediate. But the reaction needed the final treatment with TMSCHN$_2$ for the transformation of the hydroxyl group into a methoxy group.



Scheme 17. Pd-Catalysed aryl alkenylation directed by- a monophosphoric acid group

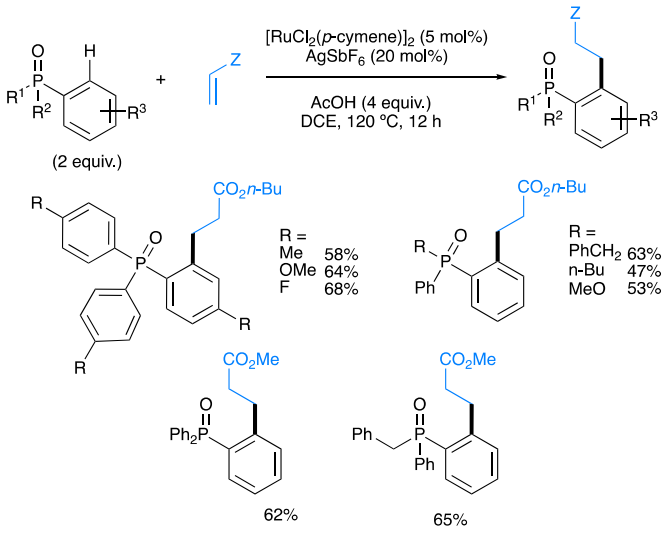
3. Alkylation of arylphosphine oxides with alkenes

During their investigation on *ortho*-alkenylation of arylphosphine oxides with alkynes using Ru(II) catalysis, Satoh, Miura *et al.* described only one example of direct alkylation by replacing the alkyne partners with *n*-butyl acrylate (Scheme 18).[14] In the presence of 1-adamantanecarboxylic acid, 33% of alkylated product is obtained in dioxane and 50% in diglyme. However, the scope of this transformation was not investigated.



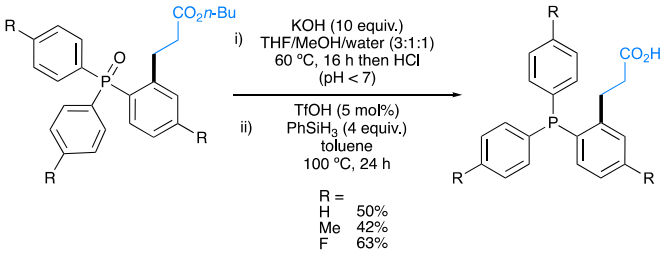
Scheme 18. Ru-catalysed *ortho*-alkylation of triphenylphosphine oxide with acrylates

In 2017, as carboxylic acids are often a catalyst partner for C–H bond functionalisations, our group investigated this alkylation reaction for the straightforward synthesis of bifunctional phosphine bearing a carboxylate function (Scheme 19).[19] We found that the $[RuCl_2(p\text{-cymene})]_2$ / 4 $AgSbF_6$ catalyst associated with simple AcOH in dichloroethane is able to promote the formation of ruthenacycle –*via* C–H bond activation at *ortho*-position of the P=O group– followed by alkene insertion and protonolysis of Ru–C bond to afford the *ortho*-alkylated arylphosphine oxide in good yields (Figure 1). To obtain a monoalkylation of one ortho C-H bond 2 equivalents of phosphine oxide need to be used. It is demonstrated that the alkylation reaction takes place without oxidant such as $Cu(OAc)_2$. Several substituted triarylphosphine oxides are *ortho*-alkylated in good yields with *n*-butylacrylate. In addition, desymmetrization of alkyl diarylphosphine oxides and methyl diphenylphosphinate was achieved using this late-stage alkylation leading to chiral phosphine oxides containing three different substituents. The reaction has been also extended to other activated alkenes.



Scheme 19. Ru-catalysed *ortho*-alkylation of arylphosphine oxides with alkenes

After production of *ortho*-alkylated of triarylphosphine oxides with acrylate, the hydrolysis of ester followed by the reduction of phosphine oxide using phenylsilane afforded the synthesis of novel bifunctional phosphine containing a pendent carboxylic group as hybrid ligands (Scheme 20).



Scheme 20. Preparation of bifunctional phosphine-carboxylate ligands

Overall, a unified mechanism for the C–H bond alkylation (and hydroarylation of alkynes) *versus* alkenylation with Ru(II) catalyst but applicable to other high valent Pd(II) and Rh(III) catalysts is depicted in Figure 1. The oxygen atom coordination of phosphine oxide leads to the 16-electron intermediate **B**, and subsequent (external) acetate-promoted deprotonation allows the formation of the 6-metallacycle **C** and RCO_2H. Coordination of alkene or alkyne and insertion into the Ru–C bond affords the intermediate **D** (with alkene) or **E** (with alkyne). In acidic media –and due to the coordination ability of the P=O bond, avoiding classical β-H elimination– proto-demetallation of **D** affords the linear alkylation product **F** and regenerates the salt Ru^{2+}. Thus, for alkylation the use of oxidant $[Cu(OAc)_2]$ is no longer required. Similarly, the complex **E** leads to the hydroarylation product **G**, *via* the protonation of the M–C bond in the presence of proton sources. On the other hand, under basic conditions the intermediate **D** undergoes a base-assisted β-H deprotonation to form the alkenylation product **F**. This deprotonation in basic medium generates M^0 species and an oxidant such as $Cu(OAc)_2$ is required to regenerated the active species Ru^{2+}.

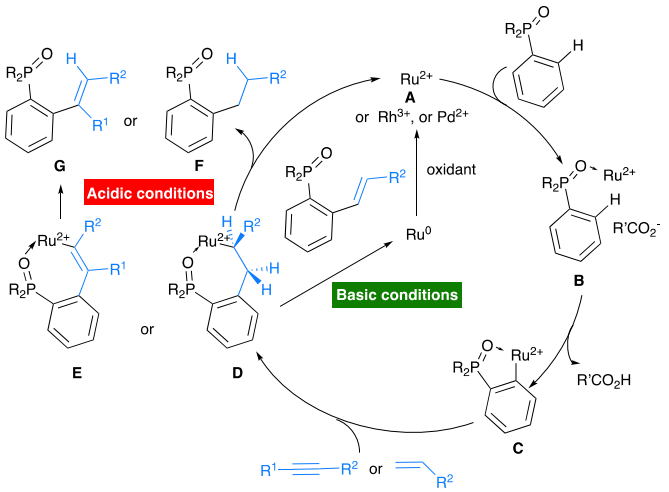
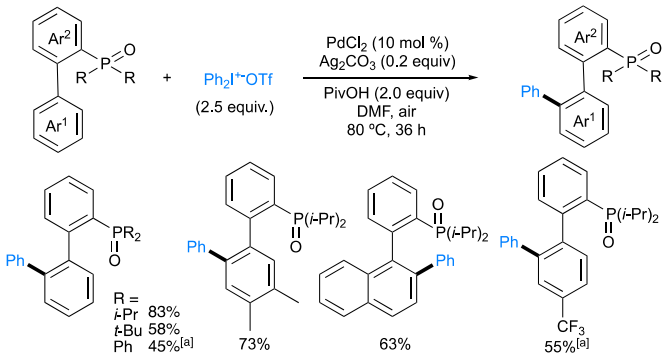


Figure 1. Unified mechanism for C–H bond functionalisation of phosphine oxides with alkynes, and alkenes.

4. Arylation of arylphosphine oxides

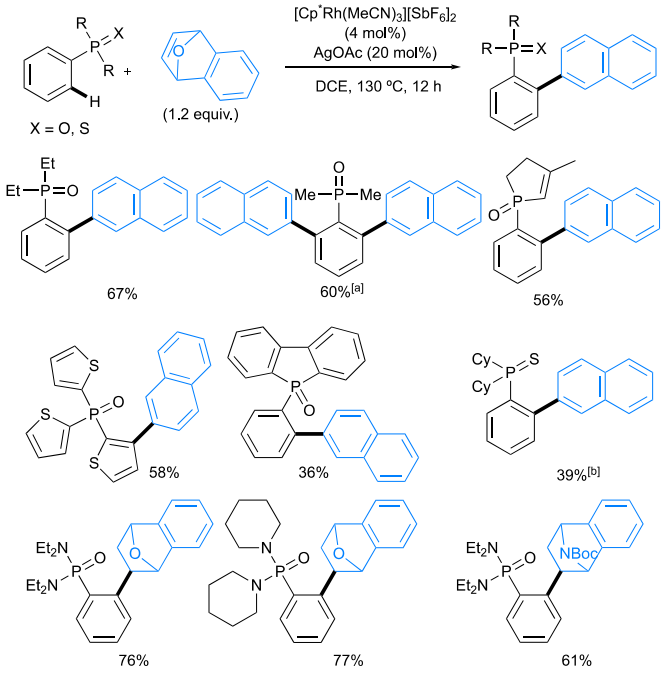
The first arylation of a biphenyl moiety directed by a $R_2P{=}O$ group was reported in 2014 by Yang's group using diaryliodonium trifluoromethyl sulphonate with the catalytic system $PdCl_2/Ag_2CO_3$/PivOH in DMF under air atmosphere (Scheme 21).[24] A variety of dialkylP=O and $Ph_2P{=}O$ directing groups allowed the C–H bond phenylation at the *ortho'*-

position, even with several substituents at *meta'* and *para'* positions. Actually, when diisopropylphenyl-phosphine oxide (thus without biphenyl group) is used, the phenylation of C–H bond did not occur, suggesting that the formation of the 5-membered cyclometallated intermediate does not take place with Pd(II) catalyst and that the regioselective formation of the 7-membered cyclometallate is rather favoured. The monoarylations of a variety of biphenyl dialkyl phosphine oxides with (mesityl)(aryl)I^+TfO^- are easily performed. The prepared polyaromatic phosphine oxides could be transformed into phosphorous(III) compounds by classical reduction with trichlorosilane in the presence of NEt_3.



Scheme 21. Regioselective monophenylation of various biphenyl C–H bonds directed by $R_2P{=}O$ groups. [a] $PdCl_2$ (20 mol %), Ag_2CO_3 (0.4 equiv) were used.

In 2015, Miura and co-workers succeeded to perform the direct functionalisation of arylphosphine oxide *ortho* C–H bond *via* the insertion of a heterobicyclic alkene such as 1,4-epoxydihydro naphtalenes leading to on dehydration formal arylation at the *ortho* position of the phosphorous directing group. The reaction is catalysed by a Cp*Rh(III) catalyst which after formation of a 5-membered cyclometallate and alkene insertion, leads to dehydrative aromatization (Scheme 22).[25] Thus, the phenyl phosphine oxides and 1,4-epoxydihydro naphtalene with the catalyst $[Cp^*Rh(MeCN)_3(SbF_6)_2]$ and AgOAc in DCE at 120 °C form *ortho*-naphtyl phenylphosphine oxides. With the less bulky $Me_2P{=}O$ group and with an excess of bicyclic alkene, the bis *ortho*-naphtylation could be achieved. $(2\text{-Thiophenyl})_3P{=}O$ derivative leads to the naphtylation of one thiophenyl group at the C2 position. The naphtylation of 5-phenyldibenzophosphole oxide occurred on the phenyl moiety, not on the dibenzophosphole ring, probably because of the easier formation of the 5-membered metallacycle intermediate. The sulphide $(Cy)_2(Ph)P{=}S$ could not be arylated under standard conditions, but by using 3 equiv of AcOH instead of AgOAc and the reaction led to 39% of arylated product. The reaction of phenylphosphonamides with the same bicyclic alkene gave the hydroarylation without the formation of biaryl product as well as with *N*-Boc bridged similar bicyclic alkene. The biarylphosphine oxides are converted into phosphine derivatives by reduction with trichlorosilane.



Scheme 22 Reaction of arylphosphine oxide derivatives with 1,4-epoxydihydro naphthalene. [a] 2 equivalents of 1,4-epoxydihydro naphtalene is used. [b] 3 Equiv. of AcOH was used instead of AgOAc.

The proposed plausible mechanism is shown on Figure 2.

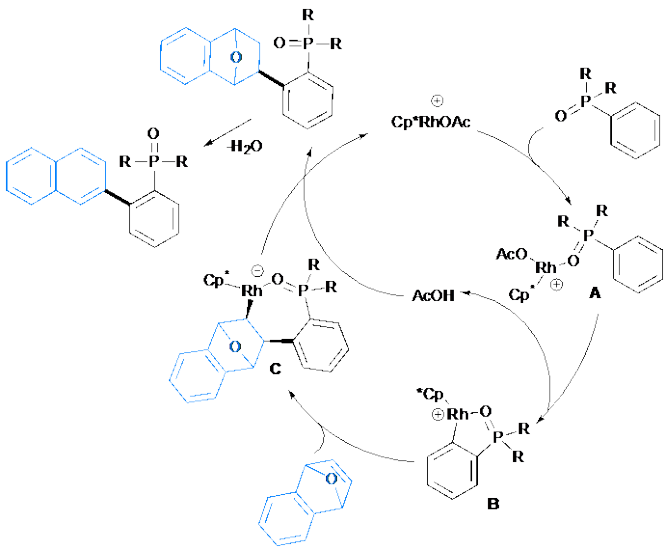
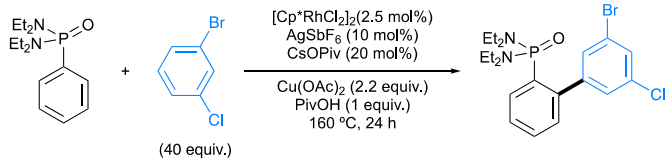


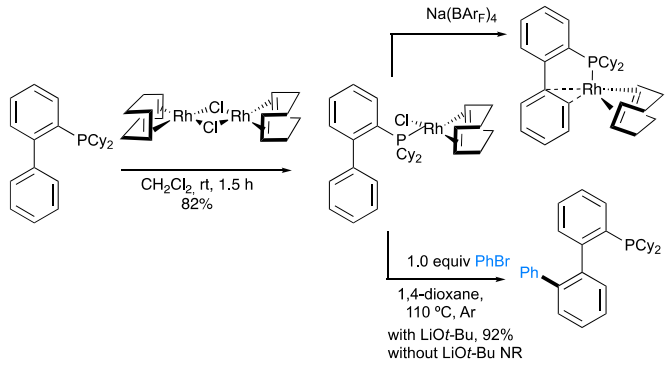
Figure 2. Mechanism for the catalysed naphtylation of arylphosphine oxides with 1,4-epoxydihydro naphthalene

Glorius and co-workers reported one example of C–H bond arylation at *ortho*-position of aryl phosphonamides through dehydrogenative C–H bond cross-coupling with 1-bromo-3-chlorobenzene (Scheme 23).[10c] The reaction operates with Cp*Rh(III) / 5 $AgSbF_6$ catalyst in the presence of stoichiometric amount $Cu(OAc)_2$ as oxidant. Only one example has been demonstrated with 1-bromo-3-chlorobenzene. The reaction occurred regioselectively at the *meta*-position of both halo substituents in a moderate yield.



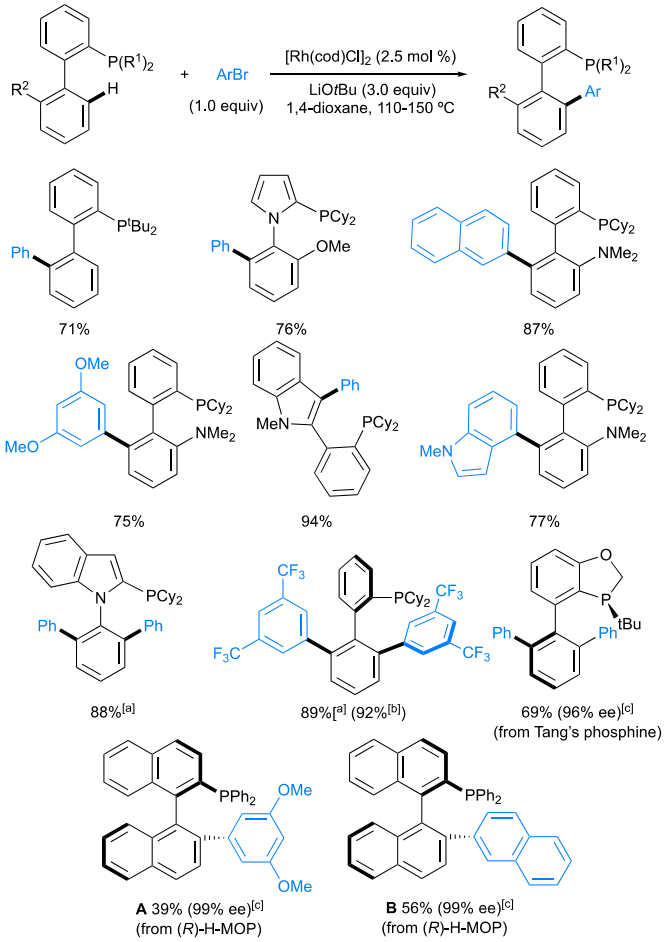
Scheme 23. Rh(III)-catalysed dehydrogenative C–H bond arylation of aryl phosphonamide

In 2017 Shi *et al.* reported the mono and bis *ortho'*-arylation of biphenyl C–H bonds directed by a phosphorous(III) group instead of phosphine oxide, on reaction with aryl bromides or chlorides but catalysed by Rh(I) catalyst. The discovery came from the observation of the stoichiometric biphenyl C–H bond cleavage from the Rh(Cl)(CyJohnPhos)(COD) complex to form a 6-membered complex as intermediate, which led to arylation with PhBr in the presence of an excess of LiO*t*Bu (Scheme 24).[26]



Scheme 24. Stoichiometric C–H bond arylation of biphenyl phosphine

The catalytic biphenyl C–H bond arylation of phosphine was thus achieved by Shi's group using 2.5 mol% of $[RhCl(COD)]_2$ catalyst with PhBr or PhCl in the presence of 3 equiv. of LiO*t*Bu at 110°C for 12h. A variety of commercially available phosphines such as Davephos or JohnPhos are arylated in high yields (Scheme 25).[26] The *ortho'*-diarylation of commercial phosphines, directed by PCy_2, PPh_2 but not $P(tBu)_2$ group are achieved using 2.4 equiv. of phenylbromide but at 140°C for 36 h in excellent yields (Scheme 25). The use of phosphine containing Rh(I) catalyst such as $RhCl(PPh_3)_3$ displayed a lower reactivity. A few examples of successive ortho'-arylations have been performed allowing the formation of mixed diarylated of the biphenyl phosphines. The direct transformation, via this arylation reaction, of chiral phosphines without racemization is achieved such as for the transformation of (*R*)-H-MOP and of the Tang's P-stereogenic phophine (Scheme 25). These new built chiral phosphines are evaluated in the enantioselective Pd-catalysed arylation of Me_2CHCO_2R and of the Rh-catalysed arylation of imines with arylstannate for which the Ar-MOP ligand **A** allowed to reach 76% yield of product with 98% enantioselectivity.



Scheme 25. Rodium(I)-catalysed arylation of commercially available phosphines. [a] Using 2.4 equiv. of ArBr; [b] Using 2.4 equiv. of ArCl, [c] using 10 equiv of ArBr.

Whereas Pd(II) catalysts favoured biphenyl C–H bond activation of biphenyl phosphine oxides[24] and Rh(I) catalysed the biphenyl C–H functionalisation of phosphines,[26] it was shown in 2017 by Yang et al.[27] that Ir(III) catalysts allow the *ortho* phenyl C–H bond functionalisation of phosphine oxides as it was also shown with Rh(III) catalysts by Miura.[25] Yang reported that *ortho* C–H bond arylation of phosphine oxides could be achieved with the catalytic system $[Cp^*IrCl_2]_2$ / 4 $AgSbF_6$ with 2,4,6-trimethylbenzoic acid (TMBzOH) additive, which allows the *ortho* C–H bond deprotonation to form a 5-membered metallacycle. The later in the presence of a diazo compound allows the carbene insertion into the C–Ir bond and tautomerization to form 2'-phosphorylbiphenyl-2-ols (Figure 3).[27]

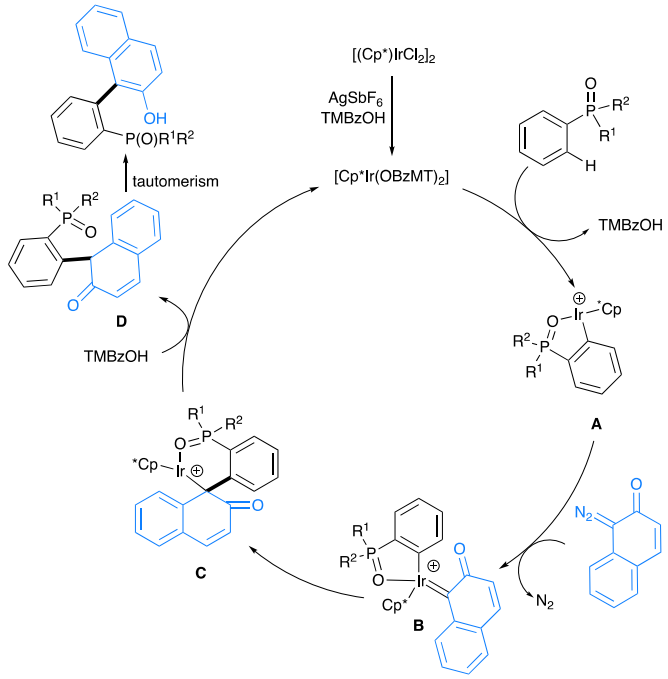
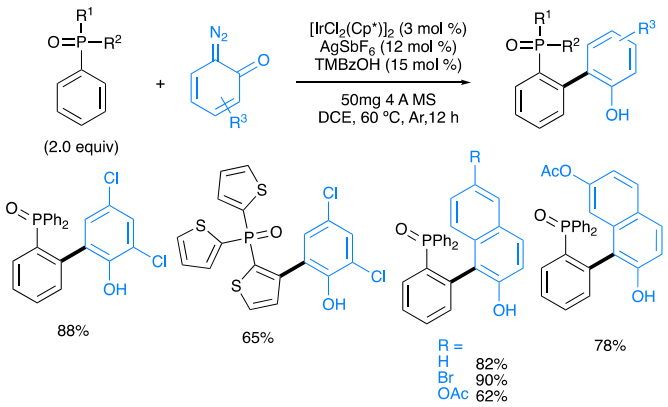


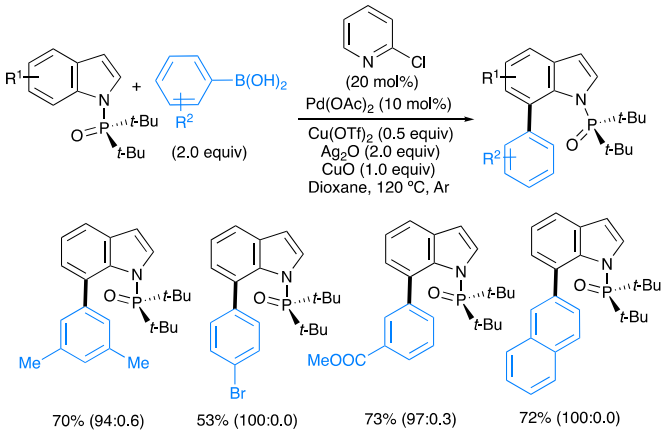
Figure 3. Proposed mechanism for the Ir(III) catalysed activation of arylphosphine oxides towards diazo compounds

Monoarylation of *ortho* C–H bond of phosphine oxides are performed with the previous catalyst with diazo derivatives of diazocyclohexa-2,4-diones and diazonaphtoquinones, in the presence of 2,4,6-trimethylbenzoic acid in dichloroethane at 60°C (Scheme 26).[27] The resulting 2'-phosphorylbiphenyl-2-ols could be transformed easily into MOB type phosphine, by $HSiCl_3$ reduction, or in Tropos-Oxazoline ligand and benzo-fused phosphine oxide.



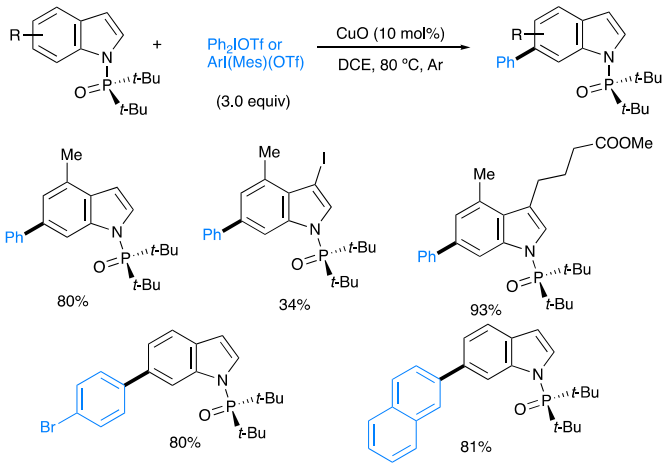
Scheme 26. Ir(III) catalysed activation of arylphosphine oxide C–H and reaction with diazo compounds

The temporary protection of the indole nitrogen with a phosphinoyl group t-$Bu_2P{=}O$ has been used by Shi for the regioselective arylation of indole at C7 position.[28] The $Pd(OAc)_2$ catalyst in the presence of 2-chloro pyridine promotes the selective C7-H bond activation, *via* the preferred 6-membered cyclometallate formation, followed by its reaction with a variety of aryl boronic acids. However, the reaction requires 2 equiv of Ag_2O plus $CuO/Cu(OTf)_2$ (Scheme 27).[28] The phosphinoyl group can be removed using $LiAlH_4$ reduction to give 7-arylindole. The *N*-phosphinoyl indole can also be alkenylated at C7 position with acrylate and $Pd(OPiv)_2$/functional pyridine.



Scheme 27. Palladium(II)-catalysed C7-H arylation of indoles directed by $R_2P{=}O$ group

The same group took profit of the same N-P(=O)tBu$_2$ directing group to arylate the indole at C6 position using copper catalysis. The arylation reagents are $Ph_2I(OTf)$ or Aryl(Mesityl)I(OTf) but the C-6 regioselectivity was obtained using CuO as catalyst at 80°C (Scheme 28).[29]



Scheme 28. Copper-catalysed C6-H arylation of indoles directed by $tBu_2P{=}O$ group

The proposed mechanism suggests a formal regioselective insertion of the C6=C7 double bond in the Ph-Cu(III) bond of intermediate (Figure 4).[29]

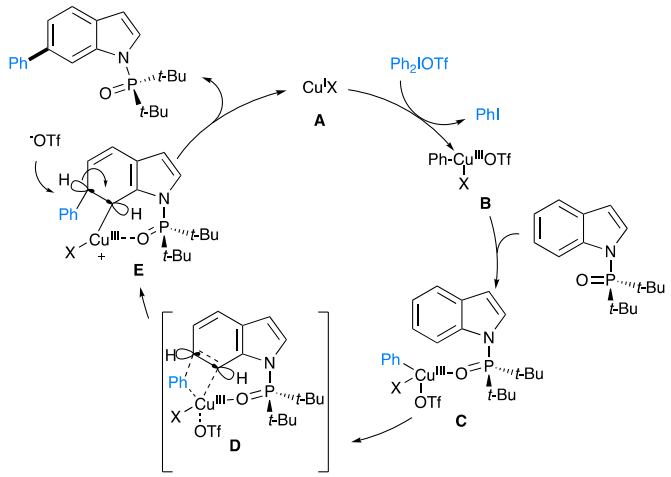
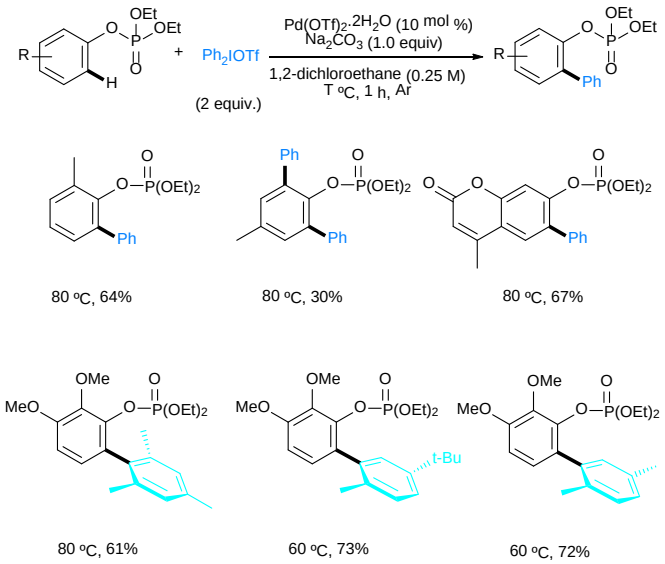


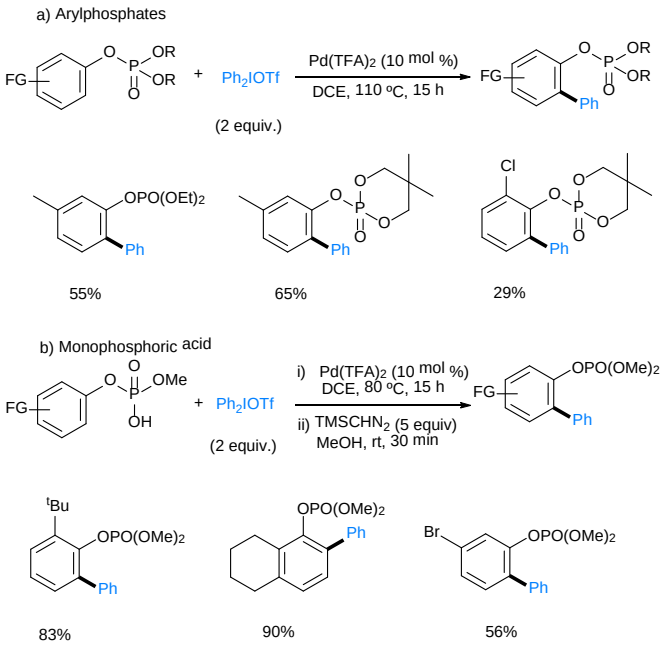
Figure 4. Proposed mechanism for Cu-catalysed C6-H arylation of indoles

In 2013 were reported several examples of arylation of ortho C-H bonds of aryl groups directed by a phosphate –O-P=O(OR)$_2$ or a phosphoamidate –NR-P=O(OR)$_2$ directing group. Thus the presence of a heteroatom between the P=O and aryl groups allows the easy formation of a 6-membered cyclometallate. However the directing groups do not give a fast access to phosphine derivatives as phosphine oxides do. Thus Moon[30] Kim[31] and Kim and Lee[32] took profit of the Pd(II) catalysed ortho C-H bond activation to perform C-H bond arylation using Ar$_2$I(OTf) reagents.

Moon et al[30] used the Pd(OTf)$_2$ catalyst for ortho arylation of arylphosphates with both Ph$_2$I(OTf) and Ar$_2$I(OTf) reagents at moderate temperature (Scheme 29)..[30] Kim et al. used Pd(O$_2$CCF$_3$)$_2$ catalyst for ortho phenylation of arylphosphonates and of aryl hydrogen phosphates with Ph$_2$I(OTf) (Scheme 30) [31].

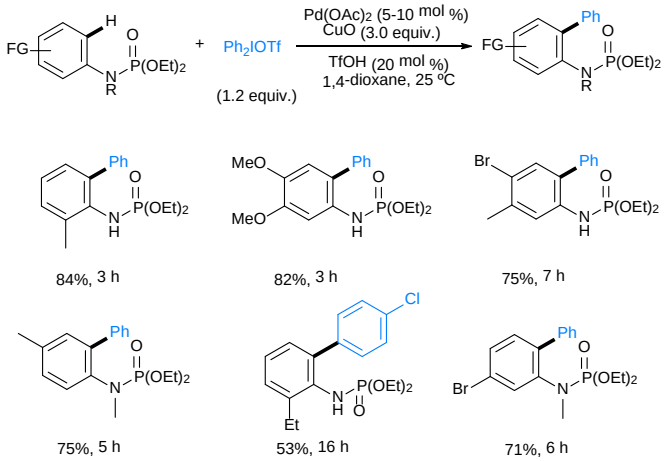


Scheme 29. . Pd(II)-catalyzed arylation of arylphosphates with diaryliodonium triflates

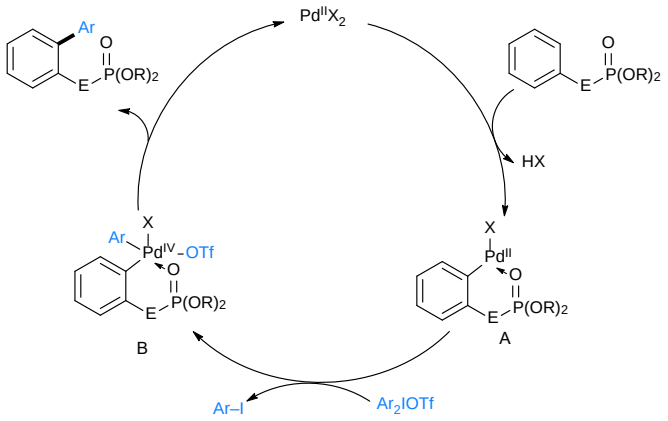


Scheme 30. . Arylation of arylphosphates and monophosphoric acids

Finally Kim and Lee performed the ortho arylation of arenes directed by a phosphoramide group with Pd(OAc)$_2$. catalyst with CuO and TfOH but at room temperature with Ph$_2$I(OTf) or Ar$_2$I(OTf (Scheme 31) [32]



Scheme 31. . Arylation of N-aryl Phosphoramidates.



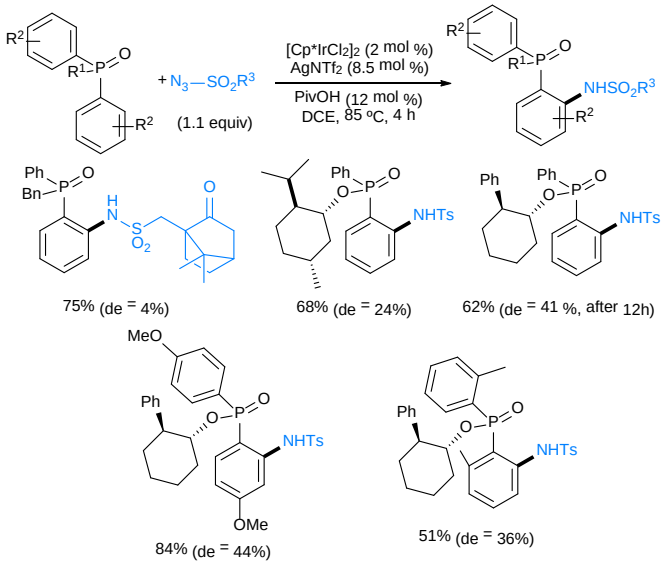
Scheme 32. . Plausible mechanism for E= O, NH, NR.

For the arylations described in Scheme 29-31 a similar plausible mechanism can be proposed based on initial coordination of the P=O oxygen atom to the Pd(II) species which promotes the ortho C-H bond deprotonation to give the 6-membered metallacycle **A**. The oxidative addition of Ar+ generates a Pd(IV) intermediate **B** which on reductive elimination gives the ortho arylated product (Scheme 32).[30-32]

Although these reactions take place under rather mild conditions due to the easy formation of a 6-membered cyclometallate intermediate, they do not offer the direct access to arylated phosphine derivatives such as benzyl and biphenyl phosphines or by reduction of functionalized phosphine oxides.

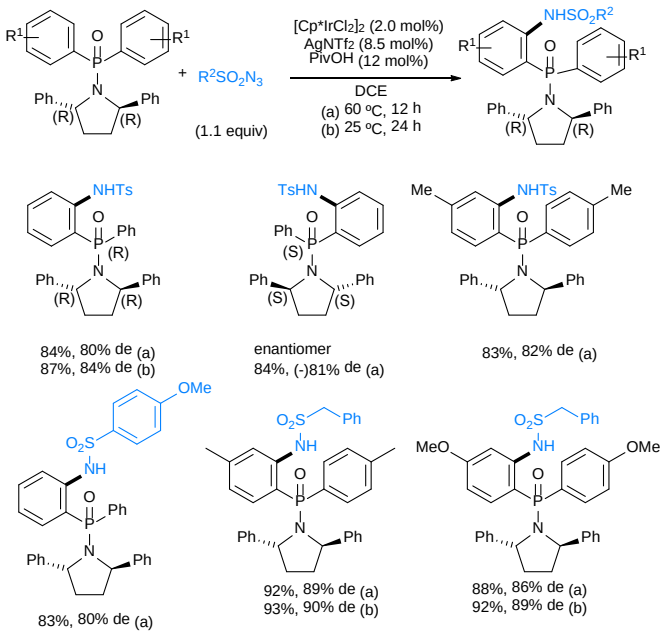
4. *Ortho*-amination of arylphosphine oxides

The catalytic amidation of arylphosphoryl C–H bonds has first been performed in 2014 by Chang *et al.* to create P-stereogenic centers.[33] Profit of the P=O directing group was taken, using an efficient Ir(III) catalyst $[Cp^*IrCl_2]_2$. Starting from $Ph_2(R^*)P{=}O$ derivative containing one chiral R* group, they are able to differentiate two phenyl *ortho* C–H bonds. It occurred *via* the expected formation of a 5-membered metallocycle, arising from C–H bond deprotonation, and followed by the amidation of the C–Ir bond with *p*-toluenesulfonyl azide. The catalytic amidation of several phosphine oxides containing a chiral group arising from chiral alcohol, such as menthol, led to good yield in the formation of aminated products with good diastereoselectivity. The nature of substituents on the phenyl groups has a strong influence on the diastereoselectivity (with chiral -2-phenyl cyclohaxanol : de = 19% for o-MeO-, 44% for p-MeO, 36% for o-Me, of 49% for Cl) (Scheme 33).[33]



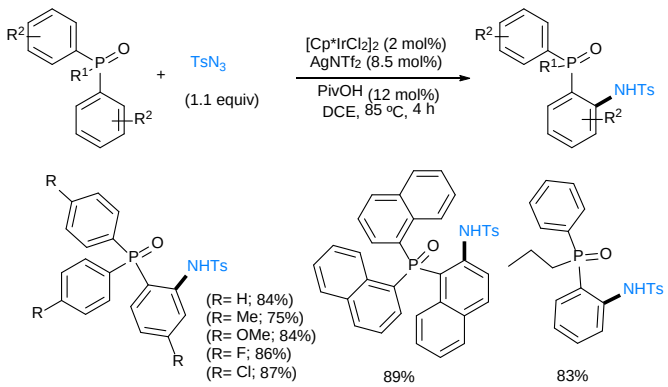
Scheme 33. Asymmetric C–H amidation of phosphine oxide aryl C–H bonds

Better amidation diastereoselectivity is obtained when the chiral group linked to the phosphorous atom has a C_2-symmetric pyrrolidine moiety (Scheme 34).[33] Thus, at 25°C or 60°C diastereoselectivities above 80% could be obtained. The diastereoselectivity is also dependent on the nature of the azide used. When one enantiomer was subjected to the standard conditions an enantiomeric aminated product was obtained with a similar *de* (-) 81% (Scheme 34) when compared to the starting enantiomer.



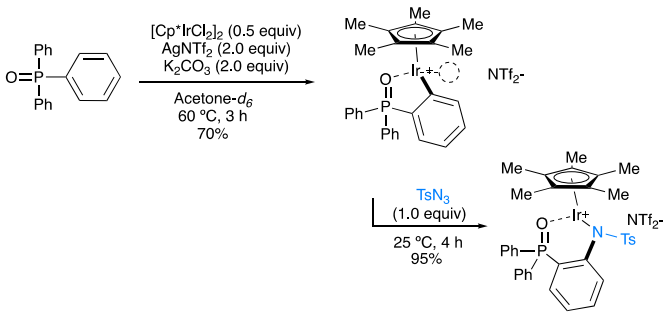
Scheme 34. Asymmetric amidation of phosphinic amides

Catalytic *ortho* C–H bond amidation of a variety of triaryl and alkyldiaryl phosphine oxides were also performed at 85°C for 4 h with TsN_3 (1.1 equiv.) and led to high yield of monoamidation product (Scheme 35).[33]



Scheme 35. Non chiral amidation of triarylphosphine oxides.

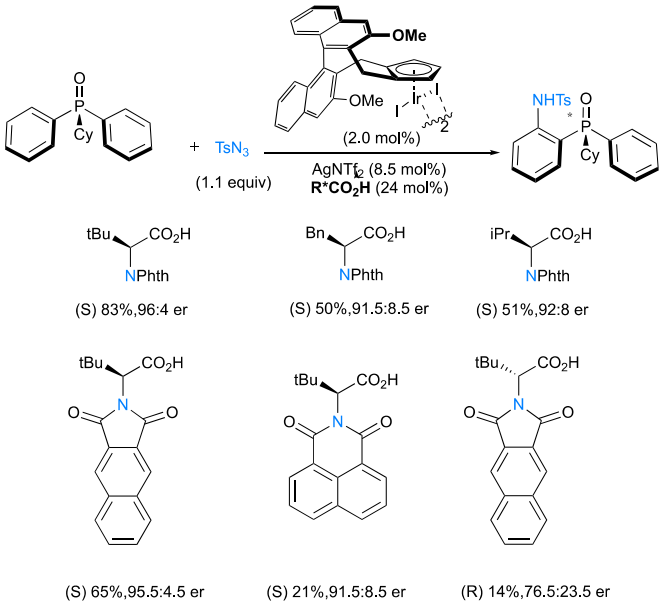
To improve the enantio or diastereoselectivity in aryl C–H bond amidation the mechanism of the amidation of phosphine oxides with azide was studied by Chang.[34] They demonstrated that the addition of 12 mol % of pivalic acid tremendously improved the catalytic efficiency of the $[IrCl_2Cp^*]_2$ / 4 $AgNTf_2$ system. They also showed, by KIE experiments, that the C–H bond cleavage is involved in the turnover-limiting step. Then, they were able to isolate and characterize the 5-membered cyclometallate from stoichiometric reaction of triphenylphosphine oxide with Cp*Ir(III) and K_2CO_3 as base. In the presence of TsN_3, such intermediate led to the insertion of the nitrene into the Ir–C bond to give the 6-membered cationic cyclometallate (Scheme 36). They also showed that the coordination of the carboxylate to the Ir(III) center favoured first the cyclometallation and that the formed carboxylic acid leads to the protodemetallation of the nitrogen containing metallacycle.



Scheme 36. Formation of Iradacycle intermediates from phosphine oxide

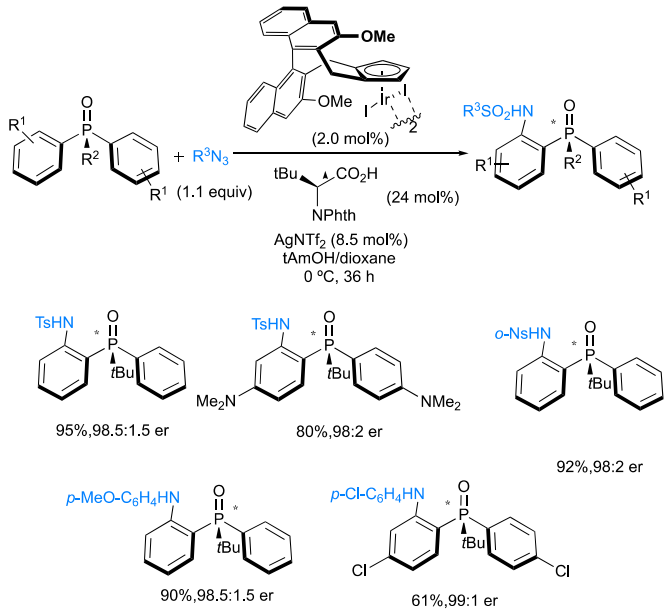
To show the influence of chiral acid on the enantioselective C–H amidation the prochiral alkydiphenylphospine oxides $Ph_2RP{=}O$ were amidated with TsN_3 in the presence of one diastereoisomer of *O,O*-dipivaloyl-L-tartaric acid. (4mol%). Very good yields were obtained >80% but with moderate enantioselectivities (ee : R= Me :11%, Benzyl: 19%, *t*-Bu: 27%, cyclohexyl: 32%). However this low asymmetric induction shows that the chiral acid additive is involved in the C–H bond cleavage and the formation of cyclometalate intermediate.

In 2017, Cramer *et al.* have reported an efficient enantioselective C–H bond amidation of phosphine oxides by taking profit of cooperative effects between a chiral carboxylic acid and a chiral Cpx-Iridium(III) catalyst.[35] They have operated with a chiral iridium(III) catalyst based on atropchiralcyclopentadienyl ligand of type $[Cp^x\text{-}IrI_2]_2$ with AgNTf, with the cooperation of a chiral amino acid derivative such as (S)-phtaloyl tert-leucine, for the amidation of *ortho* phenyl C–H bonds of alkyl$(Ph)_2P{=}O$ with TaN_3. They observed matched and mismatched effects of a variety of chiral carboxylic acids with the Ir(III) catalyst but they succeeded to obtain high yields of amidated phosphine oxides with high enantioselectivity (Scheme 37).



Scheme 37. Examples of matched and mismatched effects of chiral carboxylic acids on enantioselective amidation of phosphine oxides.

Using several azides a large variety of amidated phosphine oxides are thus obtained with high yields > 95% and with high enantioselectivity up to 99:1 using (*S*)-phtaloyl tert-leucine as a chiral partner (Scheme 38).[35] The phosphine oxides were easily transformed into borane adducts of P-chiral phosphine.[35]



Scheme 38. Examples of Ir(III) catalysed enantioselective amidation of phosphine oxides

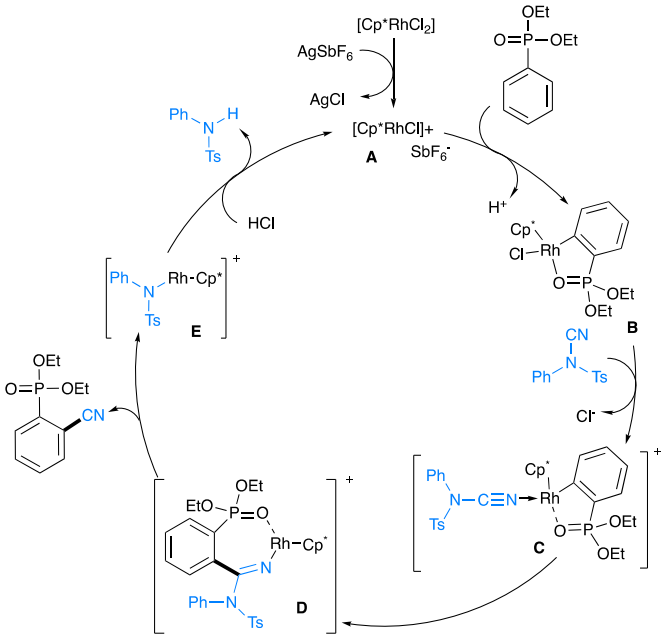
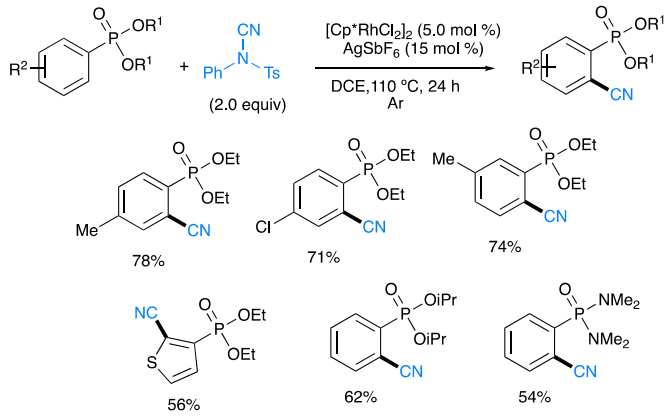


Figure 5. Proposed mechanism for the *ortho*-cyanation of arylphosphates

6. *Ortho*-Cyanation of arylphosphine oxides

Ortho C–H bonds of arylphosphates have selectively been transformed into C–CN moieties using *N*-cyano-*N*-phenyl-*p* toluenesulfonamide as cyanation reagent with $[RhCp^*Cl_2]_2$ (5 mol%), / $AgSbF_6$ (15 mol%) as catalytic system by Ding and co-workers as early as 2013 (Scheme 39).[36] *Ortho* cyanation took place on the aryl, naphtyl or 3-thienyl phosphonate in dichloroethane at 110°C with a variety of substituents. Dimethyl, diisopropyl arylphosphates and dimethylamino arylphosphate displayed similar reactivity allowing the formation of C–CN bond in good yields.

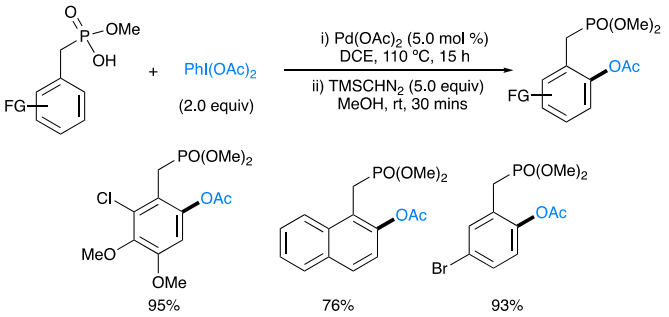


Scheme 39. Rhodium(III) catalysed *ortho*-cyanation of arylphosphates

A plausible mechanism involving first cyclometallation on C–H bond deprotonation, insertion of nitrile of the cyanation reagent into the Rh–C bond and release of the (Ph)TsN–Rh moiety are proposed as key steps. (Figure 5).[36]

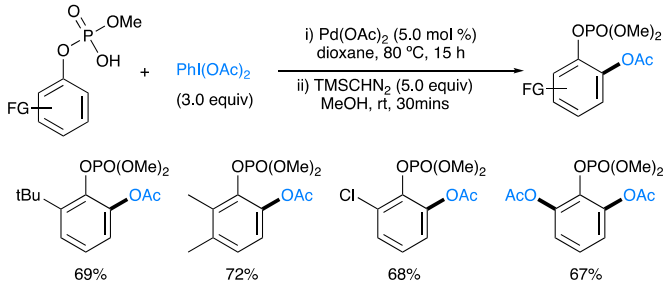
7. *Ortho*- Acetoxylation of arylphosphine oxides

In 2013, Kim *et al.* have shown that organophosphate group could direct the *ortho* C–H bond activation of the phenyl group in benzylic phosphonic acid for acetoxylation (Scheme 40).[37] Their reaction with $PhI(OAc)_2$ in the presence of $Pd(OAc)_2$ catalyst in dichloroethane at 110°C led to the acetoxylation of *ortho* C–H bonds selectively. The crude product is methylated using TMS-diazomethane to generate methyl phosphonate esters in good yields. The hydroxyl group on the phosphorous is thought to favour the *ortho* cyclometallation *via* deprotonation of the C–H bond with Pd(II)-OAc to lead the formation of a 6-membered intermediate. The resulting Pd(II)–C bond then reacts with $PhI(OAc)_2$ to give the C–OAc bond.



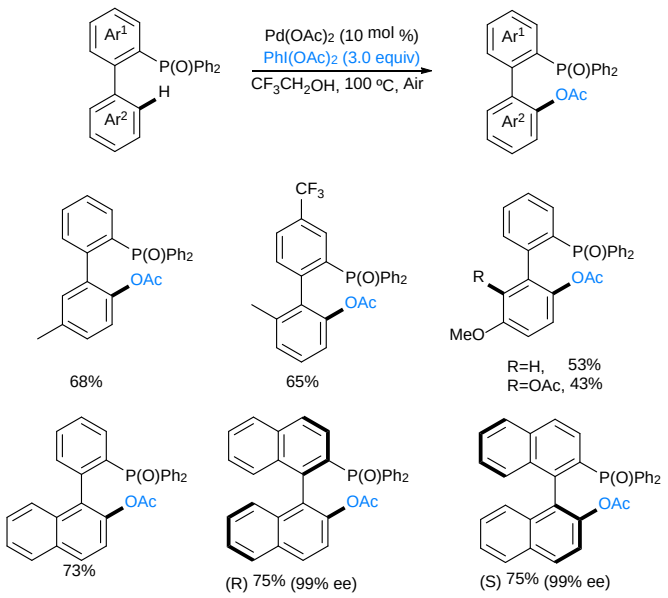
Scheme 40. *Ortho* acetoxylation of benzylic C–H bonds with monophosphoric acid directing group.

Similarly, the *ortho* C–H bond of phenylphosphoric monoacids is easily acetoxylated in dioxane under mild conditions at 80°C and tolerated a variety of substituents on the phenyl group. The products are obtained after OH methylation with TMS-diazomethane. When a large excess of $PhI(OAc)_2$ is used the *ortho* diacetoxylation could be achieved (Scheme 41).[37]



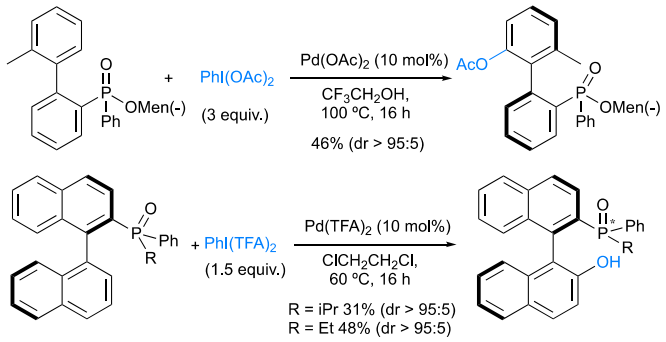
Scheme 41. *Ortho* acetoxylation of aryl C–H bonds with monophosphoric acid directing group.

In 2014 Yang et al. succeeded the acetoxylation with $PhI(OAc)_2$ of the *ortho* sp^2C-H bond of a biphenyl group directed by a $R_2P{=}O$ group in the presence of $Pd(OAc)_2$ catalyst in CF_3CH_2OH (Scheme 42).[38] The reaction proceeds via the formation of a 7-membered intermediate via C-H bond deprotonation. Diacetoxylation of *ortho* C-H bonds could be performed. More importantly the acetoxylation of each *R*- and *S*- optically pure 2-diphenylphosphine oxide-1,1'-binaphtyl leads to high yield (75%) and ee (99%) (Scheme 42). The *R*- enantiomer OAc group was transformed in 3 steps in the OMe group and thus the MeO-MOP ligand was obtained in 77% yield and 99%ee.



Scheme 42. *Pd-catalyzed Acetoxylation of ortho biphenyl C-H bonds directed by $R_2P{=}O$*

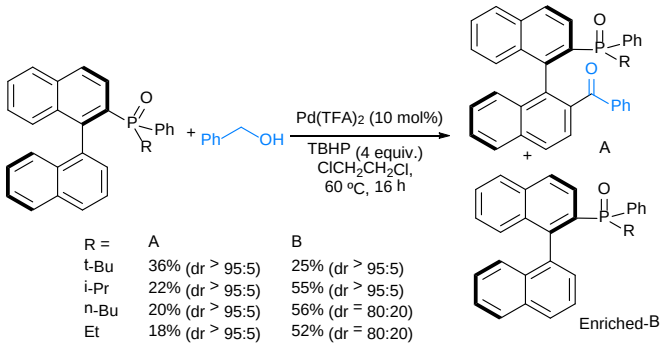
In 2015, Yang and co-worker reported the asymmetric C–H bond hydroxylation /kinetic dynamic resolution of chiral phosphine oxides (Scheme 43).[21] From (*S*)-(−)-menthyl (2'-methyl-[1,1'-biphenyl]-2-yl)(phenyl) phosphinate using $PhI(OAc)_2$ under 10 mol % $Pd(OAc)_2$ in CF_3CH_2OH at 100°C, *ortho'*-C–H acetoxylation occurred in 46% yield with excellent diastereomeric ratio (dr >95:5). Then, the authors have shown that the combination of the axially chiral substrates induced the kinetic resolution with C–H activation to construct synthetically useful axially chiral scaffolds. Indeed, when they used the axially chiral substrates, such as (*R*)-isopropyl (2'-methyl-[1,1'-biphenyl]-2-yl)(phenyl)phosphine oxide and (*R*)-ethyl (2'-methyl-[1,1'-biphenyl]-2-yl)(phenyl)-phosphine oxide, to the C–H hydroxylation, the corresponding products were obtained with moderate yields and excellent diastereoselectivity leading axially chiral phosphine oxide ligands via one step (Scheme 43).[21]



Scheme 43. Pd-catalysed *ortho'*- asymmetric C–H bond hydroxylation of enantiopure biphenyl phosphine oxides

7. *Ortho*- acylation of arylphosphine oxides

In addition to C–H bond alkenylation (Scheme 13) and hydroxylation (Scheme 43), Yang and co-workers also reported the kinetic resolution of (*R*)-alkyl (2'-methyl-[1,1'-biphenyl]-2-yl)-(phenyl)phosphine oxides through C–H acylation (Scheme 44).[21] The reactions are carried out in the presence of 10 mol% palladium catalyst associated to 4 equivalents of peroxide such as TBHP (tert-Butyl hydroperoxide) and displayed the highest diastereoselectivity and good yields for both of product **A** and recovered starting materials **B** when the phosphine oxide bears a bulky substituent (*t*-Bu or *i*-Pr).

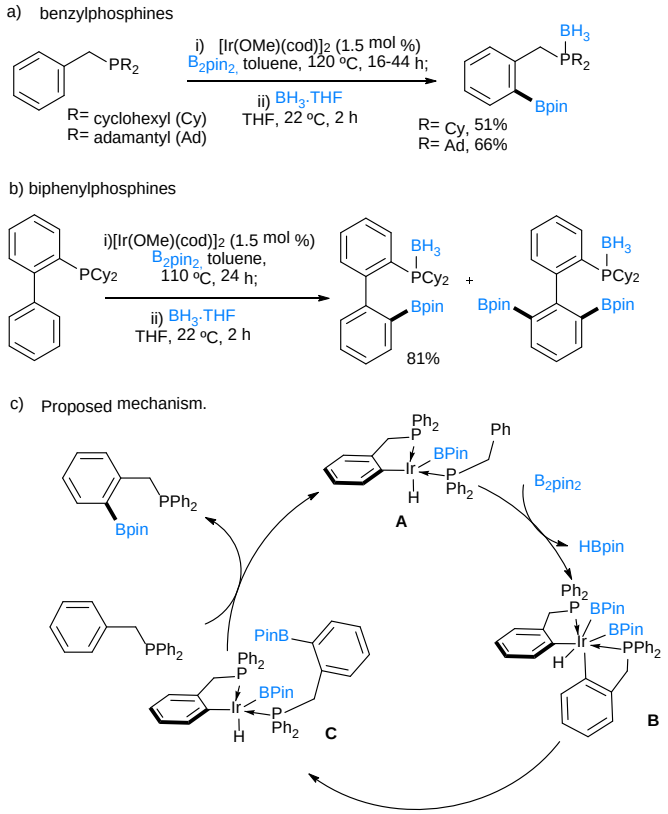


Scheme 44. Kinetic resolution (*R*)-alkyl (2'-methyl-[1,1'-biphenyl]-2-yl)-(phenyl)phosphine oxides through Pd-catalysed C–H acylation

8. Ortho borylation of benzyl and diphenyl phosphines.

In 2014 Clark et al.[39] reported the direct iridium(I)-catalyzed borylation of benzyl phosphines without initial formation of phosphine oxide as the ortho C-H bond activation in that case involves a 5-Membered cyclometallate intermediate. The reaction is catalyzed by $[Ir(OMe)(cod)]_2$ in the presence of B_2pin_2 The resulting borylated phosphines are isolated as their borane complex (Scheme 45a)).[39] Mono ortho borylation is selectively performed. As expected triphenylphosphine was unreactive due to the difficulty to generate a 4-membered intermediate. By contrast the biphenyl

group of 2-dicyclohexylphosphino) biphenyl could be directly mono borylated (Scheme 45b)[39]. At 150°C for 3 days this later phosphine led to 97% conversion with a 40/60 ratio of mono/diborylated biphenyl.



Scheme 45. Ortho borylation of benzylic and biphenyl phosphines

The proposed mechanism involves the formation from $[Ir(OMe)(cod)]_2$ of an Ir(III) cyclometallated intermediate A giving B on B_2pin_2 addition, followed by C-B bond formation leading to C. Decoordination of borylated phosphine and addition of benzylphosphine regenate the intermediate A. (Scheme 45c)[39].

Conclusion

Recent advances in transition metal-catalysed C–H bond activation/functionalisation of organophosphorus compounds have greatly impacted synthetic strategies and design of new phosphine ligands. In most of the cases, phosphorus (V) derivatives (i.e., with P=O or P=S bond) have been employed to direct the *ortho* C–H bond cleavage via the formation of 5-membered cyclometallated species with, Rh(III) and Ru(II) catalysis, allowing their functionalisations into of mostly C–C, but also C–N or C–O bonds. In contrast, with palladium catalysis, the formation of 5-membered cyclometallated species seems not be favoured. When biphenyl phosphine oxide is employed, the functionalisation occurred at the *ortho'*-position, suggesting the formation of 7-membered palladacycle. One of the most straightforward strategy to modify phosphine without protection/deprotection sequence is to employ P(III) as directing group. However, such strategy has been only succesful in the case of *ortho'* C–H bond arylation or borylation of biphenyl phosphines with rhodium(I) or iridium(I) catalysts, and with bulky phosphines only. These observations open new ways in the late-stage modification of ligands. Several optically active phosphines and diphosphines have been shown to be very useful when incorporated in metal-catalysts for enantioselective transformations. The door is now opened for late-stage C–H bond modification of their phosphine oxide or sulphide derivatives to quickly produce new active chiral functional phosphines.

Conflicts of interest

There are no conflicts to declare.

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