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Copper-Catalyzed Cross-Coupling Reactions for C-P Bonds Formation

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Abstract Phosphorus compounds are important compounds in many areas. This review briefly discusses copper-catalyzed C-P bond formation reactions. In the presence of copper catalyst, various C-P bond can be formed. C-P bond formation reactions are classified based on the different hybridization of the carbon which is connected with P atom. In addition, the challenges and opportunities of these reactions are also discussed.

1. Introduction

Phosphorus compounds have broad applications in medicinal chemistry, materials chemistry, and catalysis.[1a-1g] For example, phosphorus compounds has been used widely as catalyst in asymmetric catalysis.[1h-1i] Due to their fundamental importance, various methods for construction of C–P bonds[2] has been developed. Of all the methods, the transition-metal-catalyzed cross-coupling reactions for C–P bonds formation have received more and more attentions. Pd and Ni are the most used catalyst in transition-metal-catalyzed cross-coupling reactions for preparation of C–P bond.[3] Compared with Pd and Ni, Cu is less explored in C–P bond formation. Since Cu catalyst are relatively inexpensive and less toxic, Cu-catalyzed C–P bond formation reactions has received more and more attentions. This review summaries copper-catalyzed C–P bond formation reactions in the last few years. This would be the first review especially on copper-catalyzed C-P bond formation reactions.

2. C(aryl)–P Bond Formation

C(aryl)–P bond formation is the most common reaction in C–P bonds formation reactions. Traditionally, arylphosphines[4] were prepared from the reactions of aryl-Grignard or aryl-lithium reagents with phosphine halides. But a wide variety of functional groups can not be tolerated in this method, which hinder the application of the reaction in organic synthesis. In 2003, Venkataraman[5] and co-workers reported the copper-catalyzed corss-coupling of aryl iodides with diphenylphosphine. A vatiety of functional groups were well tolerated in this method and expensive additives was not needed. A series of unsymmetrical triarylphosphines were efficiently prepared using this protocol and the reaction conditions are much less harsh than similar protocols based on phosphination (Scheme 1).

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Zu-Li Wang

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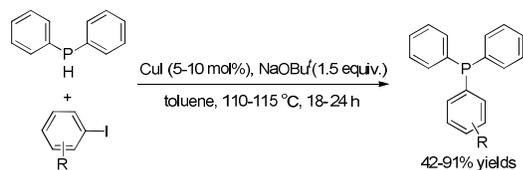
Scheme 1. Synthesis of unsymmetrical triarylphosphines.

In the presence of N, N'-dimethylethylenediamine as a ligand, Buchwald and co-workers[6] realized the copper-catalyzed C–P bond formation via direct coupling of secondary phosphines and phosphites with aryl halides in good to excellent yields. This method was of particular value given its experimental simplicity, functional group compatibility, and the low cost of the catalytic system (Scheme 2). In 2007, this method was used to synthesize the phosphinooxazoline (PHOX) ligands.[7] PHOX ligands with varied steric and electronic properties can be obtained conveniently through cross-coupling of diphenylphosphine with aryl halide.
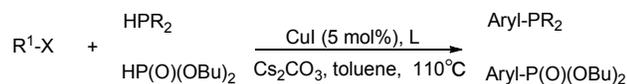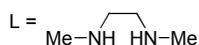
Scheme 2. Copper-catalyzed phosphination of aryl halides.

When commercially available and inexpensive proline and pipecolinic acids were used as a ligand, Fu et al. developed[8] a convenient and efficient approach for P–arylation of organophosphorus compounds containing P–H. Aryl iodides can work well in this system, but only a low yield of the product was obtained when aryl bromides was subjected to this system. In 2006, the same group[9] found that bidentate ligand, namely, pyrrolidine-2-phosphonic acid phenyl monoester (PPAPM) was also an efficient ligand for copper-catalyzed formation of C–P bonds. But aryl bromides still showed low reactivity in this system. This system was also efficient for the construction of C–N, C–O bonds (Scheme 3). This ligand showed good generality for copper-catalyzed C–P bond formation in cross-coupling reactions. In 2011, Beletskaya et al. demonstrated[10] copper-catalyzed C–P cross-coupling reactions of diethyl phosphonate with aryl iodides using 1, 10-phenanthroline as a ligand and good to excellent yields was obtained. Recently, a new ligand (S)-α-phenylethylamine[11] was explored as a ligand to promote CuI-catalyzed C–P bonds formation reactions, tertiary arylphosphine oxides could be synthesized efficiently via coupling of second phosphine oxides with aryl bromides or iodides (Scheme 4).
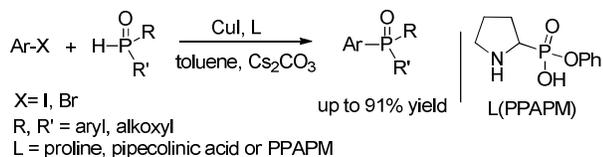
Scheme 3. Proline or pipecolinic acid-promoted copper-catalyzed coupling of aryl halides and organophosphorus compounds.
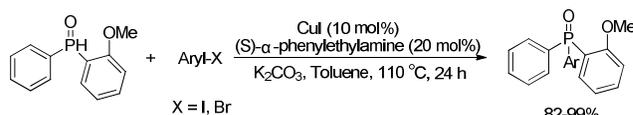
Scheme 4. Copper-catalyzed cross-coupling of aryl iodides with H-phosphonates and hypophosphite.

Without any additional ligand, Gaumont, Taillefer and co-workers[12] discovered a novel system for the syntheses of aryl phosphonates, aryl phosphinates, and aryl phosphine oxides from aryl iodides. When radical scavengers such as galvinoxyl or TEMPO was added to the system, the yield of the product did not decreased. So copper(III) intermediate was suggested in the catalytic system (Scheme 5). This result will be helpful to further probe the mechanism of the copper catalyzed C–P bond formation.
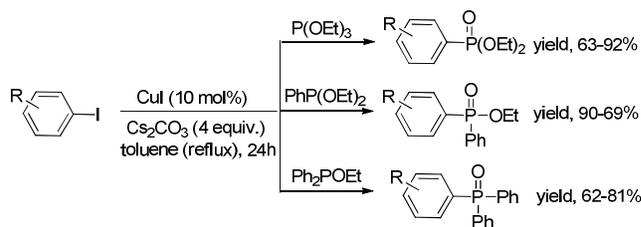
Scheme 5. Ligand-free copper-catalyzed Michaelis–Arbuzov reaction.

Under mild conditions (45-55 °C), Fu and co-workers[13] demonstrated a highly efficient method for the coupling of 2-haloacetanilides with phosphine oxides and phosphites using copper(I) iodide/N-methylpyrrolidine-2-carboxamide as the catalyst. It is worthwhile to note that whether aryl iodides or aryl bromides was well tolerated in this system, even aryl chlorides can react with organophosphorus compounds to provide the P-arylation products with 50% yields (Scheme 6). Theoretical insights into mechanisms for copper(I)-catalyzed C–P coupling of diarylphosphines with aryl halides was conducted by Zhang groups.[14] Based on determining the identity of the active catalytic species and the operative reaction mechanism for Ullmann-type P-arylation reactions, a combined effect of solvent polarity and ancillary ligand had been recognized. When phenanthroline and 1,2-ethylenediamine types of bidentate ligands was used, the active catalyst should be the neutral form LCu(I)-PPh$_2$ in nonpolar toluene, while the Cu(PPh$_2$)$_2$–anion should be significant in highly polar DMSO. However, when phosphine type ligands was used the neutral LCu(I)-PPh$_2$ complexes should be the active species in both toluene and DMSO.
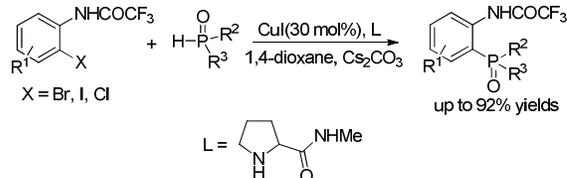
Scheme 6. N-methylpyrrolidine-2-carboxamide-promoted copper-catalyzed coupling of aryl halides with organophosphorus compounds.

Besides organohalides, arylboronic acids were also found to be good substrates in C–P bond formation reactions. Fang, Zhao and

co-workers[15] provided a novel protocol for C–P bond formation from aromatic boronic acids under mild conditions. This is the first example of copper-catalyzed synthesis of aryl phosphonates from arylboronic acids and H-phosphonate dialkyl esters. (Scheme 7)
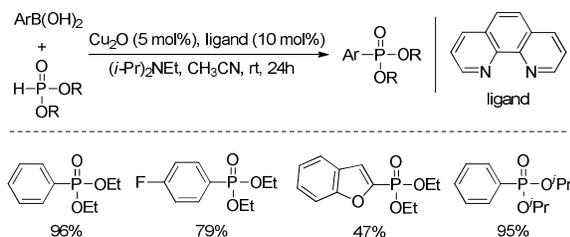
Scheme 7. Copper-catalyzed cross-coupling of arylboronic acids with H-phosphonate diesters.

Zou et.al. found that arylhydrazines were also good substrates for C–P bond coupling reactions.[16] Without any additives, the reaction of arylhydrazines with trialkylphosphites could be realized in the presence of 10 mol% CuO. Although Cu(II) could also catalyzed the reaction, the real catalyst might be Cu(I) which was reduced in situ from Cu(II) (Scheme 8). But further study was not carried out to prove the proposed mechanism.
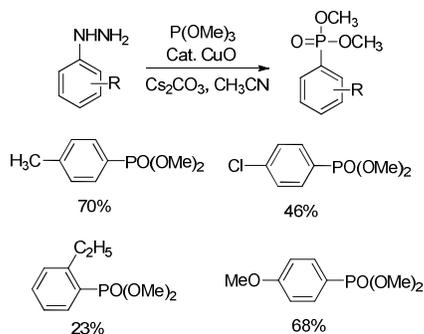
Scheme 8. CuO-catalyzed coupling reaction of arylhydrazines and trimethylphosphite.

Diaryliodonium salts, as important and valuable electrophilic arylation reagents, have attracted much attention in recent years due to their high reactivity and nontoxicity. In 2013, Tang and co-workers[17] achieved P-arylation via direct coupling of diaryliodonium salts with phosphorus nucleophiles. Products can be obtained in high yields at room temperatue in a short time of 10 min. When unsymmetrical iodonium salts were employed, nucleophilic substitution occured preferentially on the sterically hindered aromatic ring or the more electron-deficient ring (Scheme 9).
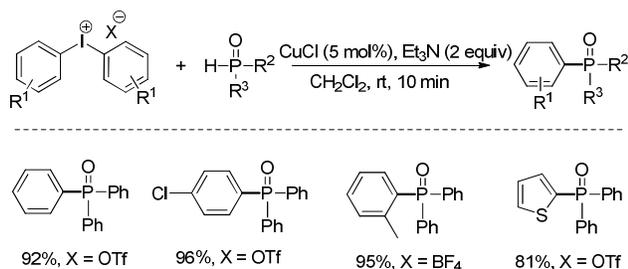
Scheme 9. Copper-catalyzed coupling of symmetrical iodonium salts with diarylphosphine oxides.

Aryl halides are the most used substrates in C(aryl)–P bond formation reactions. Compared with aryl halides, C(aryl)–H bond are less explored in C(aryl)–P bond formation reactions. Because of cost-efficient and eco-benign, it is a promising method that C(aryl)–P bond could be formed directly from C(aryl) –H bond functionalization. The first copper-catalyzed direct intermolecular arene C–H phosphorylation reaction was realized by Yu and Chen groups.[18] A variety of benzamides containing an 8-aminoquinoline moiety as a bidentate directing group were tolerated in this reaction and only the mono-substituted products was obtained. Mechanism study indicated that no radical was involved in the catalytic cycle of the phosphorylation and Cu(III) intermediates was proposed in this reaction (Scheme 10).
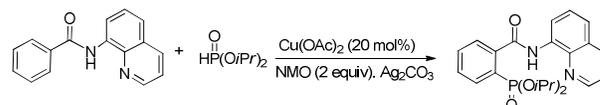
Scheme 10. Copper-catalyzed phosphorylation of carboxylic acid derivatives.

The cross-coupling reactions between indoles and H-phosphine catalyzed by copper was reported by Yang's group.[19] Different from the oxidative dehydrogenative coupling reactions reported, this reaction completely omits the oxidant and base, producing hydrogen (H_2) as the only byproduct (Scheme 11).
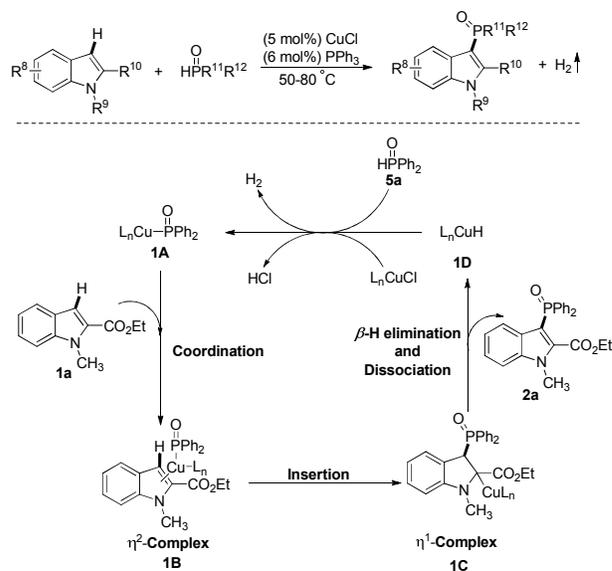
Scheme 11. CuCl-catalyzed phosphorylation of indoles.

Although there have lots of reports about Cu-catalyzed C(aryl)–P cross-coupling reactions, the mechanism of these reactions are not very clear. In 2012, Ribas and co-workers[20] disclosed that a well-defined macrocyclic aryl-CuIII complex readily reacts with $(RO)_2(O)$-PH (R =alkyl) nucleophiles to quantitatively afford the aryl dialkyl phosphonates. This work demonstrated that the CuI/CuIII redox cycle maybe incorporated in C–P cross-coupling reactions and also have instructive effect on the Cu-catalyzed C–P bonds formation (Scheme 12).
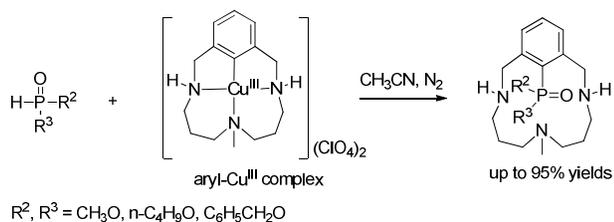
Scheme 12. Reaction of aryl−Cu(III) complex with H-phosphonate diesters

3. C(alkynyl)–P Bond Formation

Alkynylphosphanes are an attractive class of compounds in organic chemistry.[21] Beletskaya and co-workers[22] reported CuI-catalyzed cross-coupling of terminal alkynes with chlorophosphanes. Various alkynylphosphanes were obtained in high yields. (Ph$_2$PCl)$_3$CuI complex maybe incorporated in this catalytic cycle (Scheme 13).
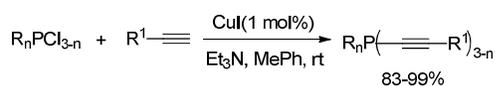
Scheme 13. Cross-coupling of terminal alkynes with chlorophosphanes.

In 2011, a new approach[23] relied on the coupling of secondary phosphine boranes with alkynyl bromides using the CuI/1,10-phenanthroline couple was presented by Gaumont *et al*. This is the first time to use a nucleophilic phosphorus derivative in C(alkynyl)–P bond formation(Scheme 14). Next year they synthesized the copper–phosphido-borane complexes and the complexes was further characterized spectroscopically and by X-ray analysis. Experimental studies[24] showed that the complexes have a catalytic activity in C(alkynyl)–P bond formation.
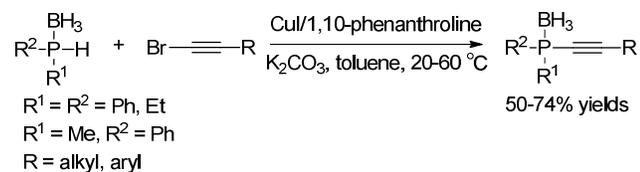
Scheme 14. Cross-coupling reaction of secondary phosphine Boranes with Alkynyl Bromides.

Transition-metal-catalyzed decarboxylative coupling reactions have received more and more attentions in recent years.[25] However, there are rare examples of C−P bond formation via metal-catalyzed decarboxylative coupling reactions. After repeated attempts, copper-catalyzed decarboxylative coupling of alkyne acid with Ph$_2$P(O)H was first achieved by Liang, Yang and co-workers.[26] Note that fatty alkyne acid also worked smoothly in this transformation (Scheme 15).
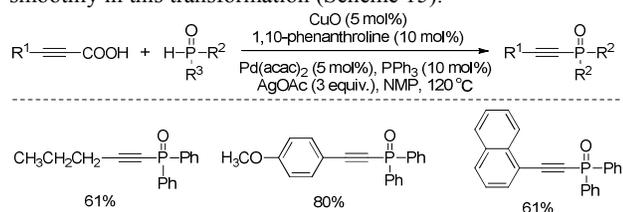
Scheme 15. Decarboxylative coupling of alkyne acid with R$_2$P(O)H.

The oxidative decarboxylative coupling of arylpropiolic acids with dialkyl H-phosphonates in water has been developed by Yang, Wu and co-workers.[27] This reaction could proceed in air at low temperature. In order to suppress the decomposition of dialkyl H-phosphonates, the addition of isopropanol was needed (Scheme 16).
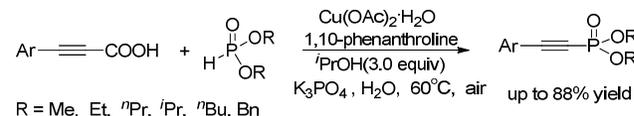
Scheme 16. Decarboxylative coupling of propiolic acids with H-phosphonates.

Without needing ligand, base, and additive, various alkynyl acids could react with H-phosphine oxides to afford E–alkenylphosphine oxides[28] in the presence of 10 mol% of CuCl. This method provided a powerful synthetic tool for simple synthesis of valuable (E)-P-alkenylated motifs (Scheme 17).
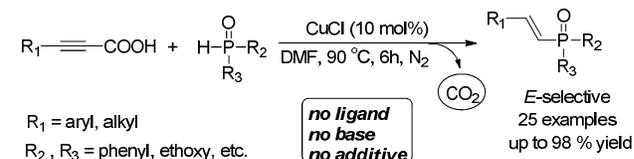
Scheme 17. Decarboxylative cross-coupling of alkyne acids with P(O)H.

Han and co-workers[29] developed an efficient copper-catalyzed oxidative coupling of alkynes with (iPrO)$_2$P(O)H. However, under similar reaction conditions, Ph$_2$P(O)H as substrate did not afford the oxidative-coupling product, because Ph$_2$P(O)H was oxidized to Ph$_2$P(O)OH (Scheme 18).
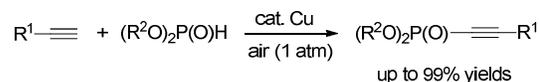
Scheme 18. Copper-catalyzed aerobic oxidative coupling of terminal alkynes with H-P(O) compounds.

Oxidative alkynylation of phosphorus-based nucleophiles with copper acetylides was achieved by Evano and co-workers.[30] A brief optimization revealed that the reaction was best performed using N-methylimidazole as the ligand in DMF at room temperature and under an atmosphere of oxygen. The presence of a free alcohol was more detrimental in this case, which might be due to a side reaction with excess diisopropyl phosphite (Scheme 19). Mechanistic study showed that dioxygen play an important role in this type reaction.[31] Dioxygen was activated by Cu(I) species to form η1-superoxocopper(II), η2-superoxocopper(III), μ-η2:η2-peroxodicopper(II), and bis(μ-oxo)dicopper(III) complexes. Then proton transfer from the phosphite to the bridging oxygen atom leads to the formation of a P−C bond.

$R^1\!\!=\!\!=\!\!Cu$ + H–P(=O)(R^2)(R^3) $\xrightarrow{\text{DMF, O}_2\text{, rt}}$ $R^1\!\!=\!\!=\!\!$P(=O)(R^2)(R^3)

86%   71%

65%   87%
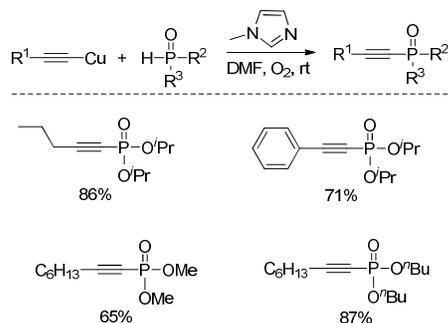
Scheme 19. Oxidative cross-coupling of phosphite with copper(I) acetylides.

4. C(alkenyl)–P Bond Formation

Vinylphosphonates are of great importance[32a] in synthetic chemistry where they are commonly used in the preparation of carbocyclic and heterocyclic compounds. As early as 1998, Ogawa *et al.* prepared series of vinylic and arylic phosphonates and phosphonic bis(diethylamides)[32b] from the corresponding bromides in the presence of copper. It is noteworthy to note that diphenyl 2-(4-dimethylaminophenyl)ethenylphosphonate exhibited strong second harmonic generation (SHG) activity, the efficiency being 13 times greater than that of urea. In 2003, Buchwald *et al.* described[33] copper-catalyzed coupling of secondary phosphines and phosphiteswith vinyl halides. Both vinyl iodides and vinyl bromides could react smoothly in this reaction.

Vinyliodonium tetrafluoroborates[34] which is a readily available reagent could react with H-phosphonates to construct 2-arylvinylphosphonates. Considering the very mild conditions of the reaction, phosphorus diastereomers could be prepared using this method (Scheme 20).

82%   66%   76%
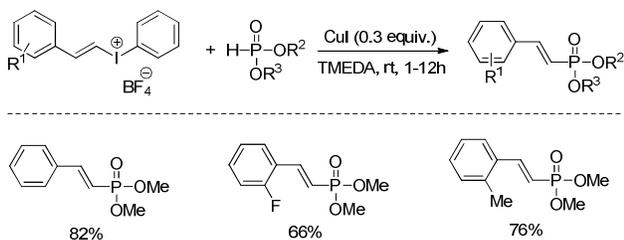
Scheme 20. Synthesis of dialkyl 2-arylvinylphosphonates.

As was mentioned aboved, alkynyl acids was good substrated to construct C–P bonds via decarboxylative coupling reactions. Besides alkynyl acids, alkenyl acids[35] was also good partner in copper-catalyzed decarboxylative coupling reactions with Ph$_2$P(O)H to form C–P bonds. This reaction exhibited the best regio- and chemoselectivity reported so far for C–P coupling (Scheme 21).

94%   78%   50%
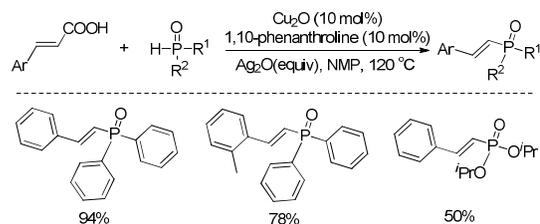
Scheme 21. Decarboxylative coupling of alkenyl acids with Ph$_2$P(O)H.

A new procedure for the preparation of E-1-alkenylphosphonates through copper-mediated cross-coupling between 1,1-dibromo-1-alkenes and dialkyl phosphites is reported.[36] This method has the advantageous feature that it starts from readily available 1,1-dibromo-1-alkenes which act as attractive synthetic equivalents of E-alkenyl bromides. But the loading of CuI was a little high and the yields of the reaction still need to be improved (Scheme 22). The crossing-coupling parter alkenyl bromides was formed by reduction of ,1-dibromo-1-alkenes, then the final product was obtained from the reaction of dialkyl phosphites and alkenyl bromides.

60%   84%   59%
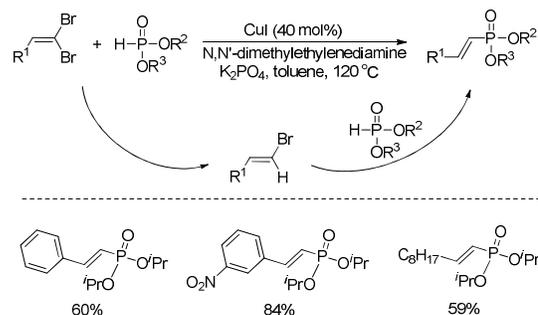
Scheme 22. Cross-coupling of 1,1-dibromo-1-alkenes with dialkyl-phosphites.

The aerobic oxidative coupling of Cu/triazole complex with H-phosphonates was disclosed in 2013 by Li and Zhang groups.[37] It is worthwhile to note that the reaction was conducted at room temperature. This reactions showed high regioselectivity and efficiency providing provides a facile new protocol for the preparation of phosphorus compounds in mild conditions. But the yield was moderate (Scheme 23). At present, the direct coupling of C(alkenyl)–H bond with phosphorous compounds has not been reported. It is an appealing target deserving our endeavor.

R, R' = akyl, aryl, ribosyl   68–85% yield
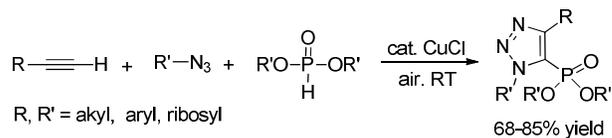
Scheme 23. Copper-catalyzed three-component reaction (CuAA[P]C reaction) of terminal alkynes, azides, and H-phosphonates.

5. C(alkyl)–P Bond Formation

In 2010, Glueck, Rheingold and co-workers[38] synthesized the intermediates which are incorporated in copper-catalyzed cross-coupling of diphenylphosphine with PhCH$_2$Br, then they

investigated the mechanism of this reaction. A proposed mechanism for catalytic P–C bond formation was proposed: deprotonation of the cationic diphenylphosphine complex [Cu(triphos)-(PHPh$_2$)][PF$_6$] by NaOSiMe$_3$ to yield the phosphide complex Cu(triphos)(PPh$_2$). Then nucleophilic attack on the substrate (benzyl halide) yields the tertiary phosphine complex. A novel approach for the alkylation of H-phosphonates and diphenylphosphine oxide using N-tosylhydrazones as new alkyl reagents has been established by Tang and co-workers. [39] Without any ligands, this reaction could afford the corresponding coupled alkylphosphonates in good to excellent yields. Alkylphosphonates can also be prepared in a one-pot directly from carbonyl compounds without the isolation of tosylhydrazone intermediates (Scheme 24).
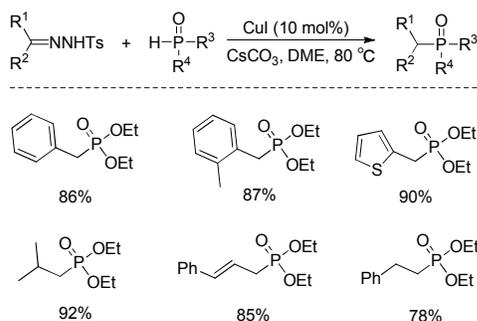
Scheme 24. Copper-catalyzed coupling of H-phosphonate with N-tosylhydrazones.

In 2013, similar catalytic system[40] was described by Liang *et al.* In the present of CuI, phosphine oxide derivatives could be prepared smoothly utilizing N-tosylhydrazones as readily available alkylating reagents(Scheme 25). An insertion of copper carbene into P-H bond of H-phosphorus oxides was proposed in this reaction mechanism (Scheme 26). The substrates for C(alkyl)–P bond formation are not explored enough at present. It is interesting to note that other more accessable substrates such as C(alkyl)–H or C(alkyl)–X will be used for C(alkyl)–P bond formation in future.
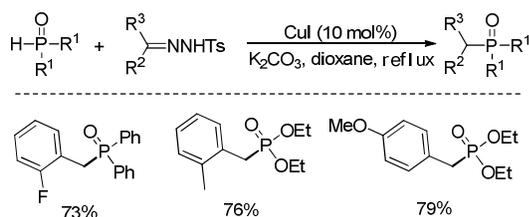
Scheme 25. The copper-catalyzed P-alkylation using N-tosylhydrazones.
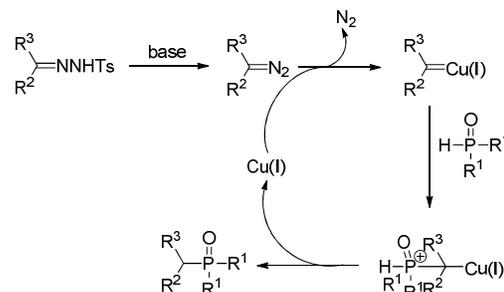
Scheme 26. Proposed mechanism of the reaction.

6. Conclusion

In conclusion, great progresses have been made in copper-catalyzed cross-coupling reactions for C–P bond formation. Various organophosphorus with good functional group compatibility can be obtained efficiently. It is believed that copper-catalyzed cross-coupling reactions for C–P bond formation will play an important role in organic transformations.

Although great advances has been achieved, challenges still remain: firstly, the substrate scopes of reactions are still limited, aryl iodides are the most used substrates in this reaction, however, the more available and cheaper organic bromides, organic chlorides and carboxylic acids were not explored enough; Secondly, the copper-catalyzed cross-coupling of C-H bond with organophosphorus to construct C-P bond via C-H bond activation was also deserve our more attention; Thirdly, asymmetric copper-catalyzed C–P bond formation catalyzed by chiral catalyst is an very interesting and important subject; Finally, the mechanism of these reactions is in need of further study, mechanism study will help us to achieve more successful C–P bond formation.

It would be a pleasure for us to see that this review will create keen interest among the wide readership of this journal and result in further focused research to meet some of these aforementioned challenges in the future.

Acknowledgements

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