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Catalytic synthesis of sulfur and phosphorus compounds *via* atom-economic reactions

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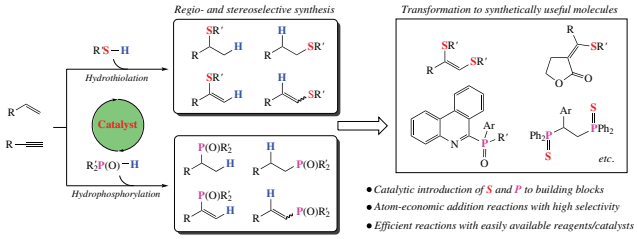
This mini-review focuses on addition reactions, as atom-economic reactions, employed for the preparation of organosulfur and organophosphorus compounds. For synthesis of organosulfur compounds, hydrothiolation of carbon–carbon unsaturated bonds is the primary focus. Concerning organophosphorus compounds, the main focus will be recent metal-catalyzed hydrophosphorylations, which include cyclization and bisfunctionalization reactions.



Keywords: addition reaction, organosulfur compounds, organophosphorus compounds, transition-metal-catalyzed addition.

Introduction

Organosulfur and organophosphorus compounds have diverse applications as polymer materials, electronic materials, and tools that control physiological activities, among others. Therefore, efficient methods for their synthesis are continually required, especially in recent years, due to increasing demands for related products. The addition reaction is theoretically an efficient reaction with high atom economy. Transition metal catalysts have expanded the diversity of addition reactions, and a plethora of transition-metal-catalyzed addition reactions have been reported to date.[1–3] However, the development of transition-metal-catalyzed addition reactions of organosulfur and organophosphorus compounds is more recent than that of other elements, because the high coordination number of the reactants was not favorable. Since their discovery, addition reactions of organosulfur and organophosphorus compounds have been recognized as a fundamental technology, and research in this area is ongoing.[4–6] This mini-review focuses on recent catalytic reactions of organosulfur and organophosphorus compounds.

Atom-economic hydrothiolation of unsaturated bonds and related reactions

Organosulfur compounds have generally been regarded as catalyst poisons, and therefore, transition-metal-catalyzed reactions of organosulfur compounds remained undeveloped for a long time. In the early 1990s, Kuniyasu and Ogawa reported the palladium-catalyzed bisthiolation[7] and hydrothiolation[8] of alkynes using organic disulfides and thiols, respectively, which

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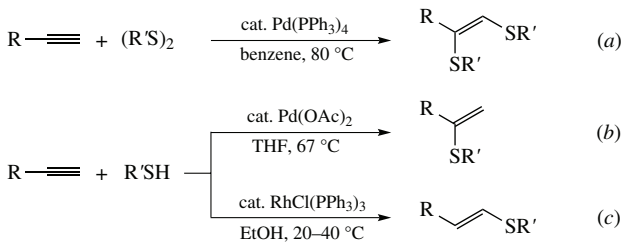
afforded a series of vinyl sulfides with high atom-efficiency. The $Pd(PPh_3)_4$-catalyzed bisthiolation of alkynes proceeds stereoselectively, *via syn*-addition of disulfides [Scheme 1(*a*)], whereas the $Pd(OAc)_2$-catalyzed hydrothiolation of alkynes affords Markovnikov adducts regioselectively [Scheme 1(*b*)]. In 1999, Ogawa reported a rhodium-catalyzed hydrothiolation of alkynes, which proceeds with opposite regioselectivity to afford anti-Markovnikov adducts [Scheme 1(*c*)].[9]



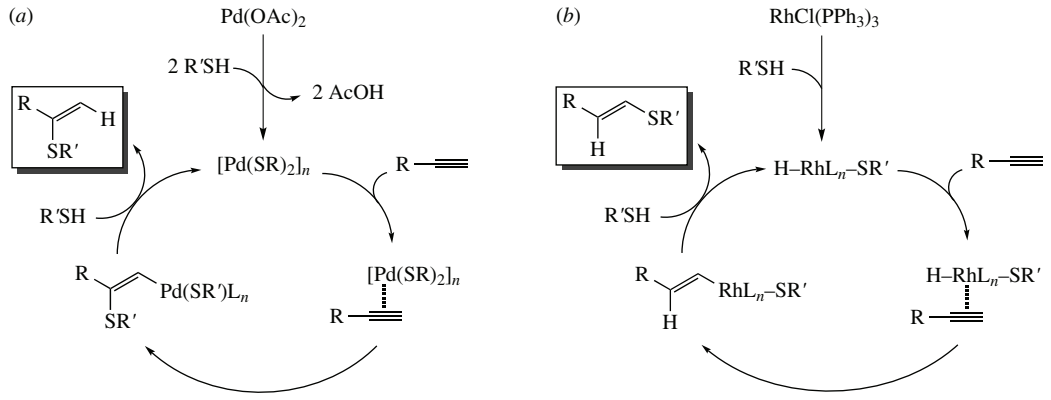
Scheme 1 Breakthrough reactions in transition-metal-catalyzed thiolation.

In Markovnikov-type hydrothiolation, palladium sulfide, $[Pd(SR')_2]_n$, is formed as a key intermediate by the reaction of $Pd(OAc)_2$ with R′SH; subsequent regioselective thiopalladation of alkynes and protonation leads to Markovnikov-type vinyl sulfides [Scheme 2(*a*)]. Ananikov and Beletskaya determined the structure of palladium sulfide and clarified its catalytic activity toward alkyne hydrothiolation.[10] In contrast, anti-Markovnikov hydrothiolation proceeds *via* the oxidative addition of a thiol to a Rh^I catalyst, analogous to $RhCl(PPh_3)_3$, to generate the H–RhL_n–SR′ species. Alkynes undergo hydrorhodation regio- and stereoselectively, and reductive elimination provides anti-Markovnikov *Z*-adducts with good selectivity [Scheme 2(*b*)].

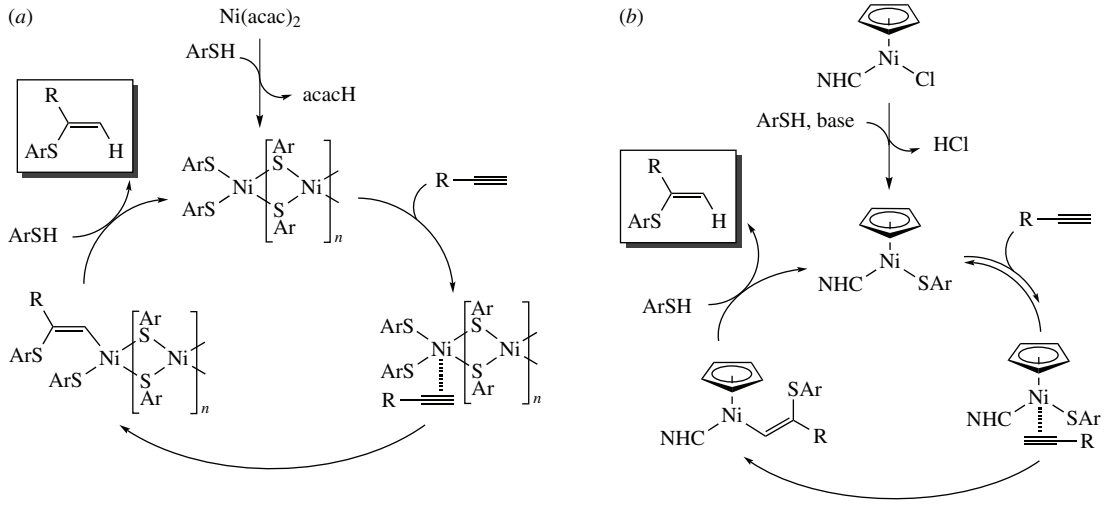
Following these pioneering studies, a variety of metal complexes have been employed for catalytic hydrothiolation, some with regio- and stereocontrol. In particular, alkyne hydrothiolation provides a convenient atom-economic synthesis of vinyl sulfides. In the mid- 2000s, Ananikov and Beletskaya developed a convenient nickel-catalyzed hydrothiolation of alkynes.[11–16] The use of inexpensive and readily available nickel(II) acetylacetonate, $Ni(acac)_2$, achieves eco-friendly, large scale synthesis of vinyl sulfides [Scheme 3(*a*)]. In addition, they were the first to demonstrate the utility of N-hererocyclic carbines (NHCs) as ligands for catalytic hydrothiolation [Scheme 3(*b*)].[13]

Subsequently, several metal complexes bearing NHC ligands have been reported to catalyze the regioselective hydrothiolation of alkynes. In general, NHC ligands are bulky, strong electron-donors, and can accelerate the dissociation of a ligand in the *trans* position. Based on these characteristic features of NHC ligands, Castarlenas was able to control the regioselectivity of alkyne hydrothiolation by the selection of ligands on the rhodium–NHC catalyst (Scheme 4).[17–19]

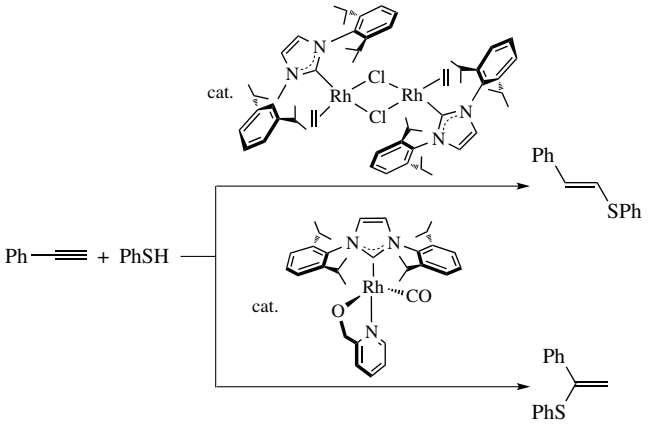
Ananikov reported that the readily available Pd–NHC complex, (IMes)Pd(acac)Cl, is an efficient catalyst for alkyne hydrothiolation, delivering Markovnikov-type vinyl sulfides, starting from tertiary, secondary, or primary aliphatic thiols, as well as aromatic thiols [Scheme 5(*a*)].[20] Yang and Rioux prepared a silica-supported Cu–NHC complex, which could be employed as a low-cost heterogeneous catalyst for alkyne hydrothiolation to afford anti-Markovnikov-type vinyl sulfides [Scheme 5(*b*)].[21]



Scheme 2 Reaction mechanisms of hydrothiolation of alkynes using $Pd(OAc)_2$ or $RhCl(PPh_3)_3$ catalyst.



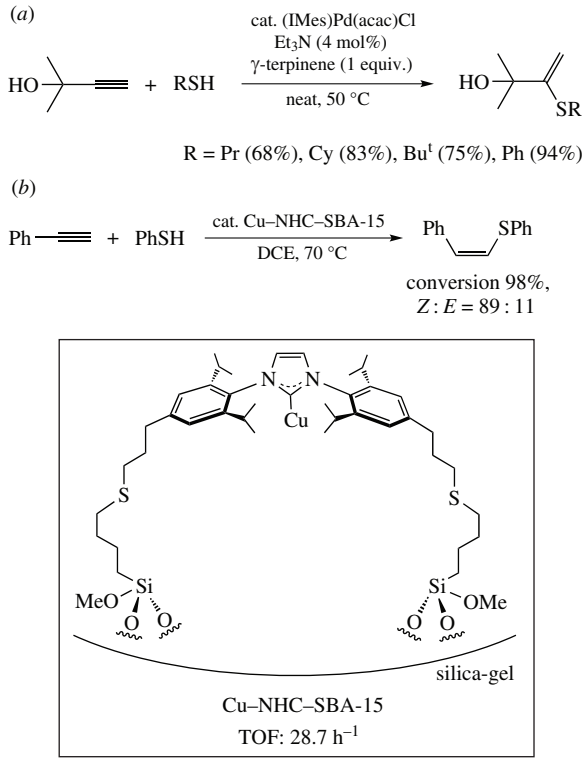
Scheme 3 Nickel-catalyzed hydrothiolation of alkynes.



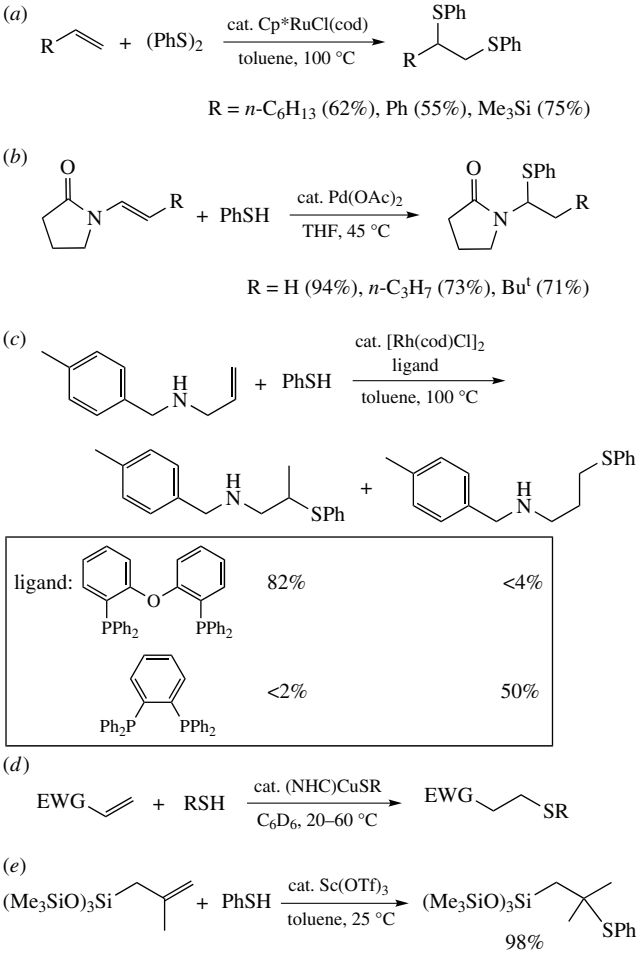
Scheme 4 Rh–NHC complex-catalyzed regioselective hydrothiolation of alkynes.

Love found that the cationic rhodium complex, Tp*Rh(PPh$_3$)$_2$ [Tp* = hydrotris(3,5-dimethylpyrazolyl)borate], catalyzed Markovnikov-selective hydrothiolation of alkynes,[22–25] in contrast to RhCl(PPh$_3$)$_3$-catalyzed anti-Markovnikov selective hydrothiolation.[26] Catalytic hydrothiolation of alkynes using several early transition metal catalysts, such as organozirconium, lanthanide, and actinide complexes, are reported by Marks to regioselectively produce Markovnikov-type vinyl sulfides.[27–30] Additionally, catalytic hydrothiolation has been found to proceed in the presence of Fe,[31,32] In,[33–36] Cs[37] and Ca[38] catalysts.

As mentioned previously, interest in transition-metal-catalyzed alkyne hydrothiolation has increased in recent years, resulting in the development of a number of synthetically useful transformations. In sharp contrast, examples of transition-metal-catalyzed hydrothiolation of alkenes are very limited, as the poor coordination ability of alkenes renders this reaction challenging. A pioneering study on related catalytic alkene bisthiolation using a ruthenium catalyst has been reported by Kondo and Mitsudo [Scheme 6(*a*)].[39] Regarding alkene hydrothiolation, heteroatom-



Scheme 5 Metal–NHC complex-catalyzed hydrothiolation of alkynes.

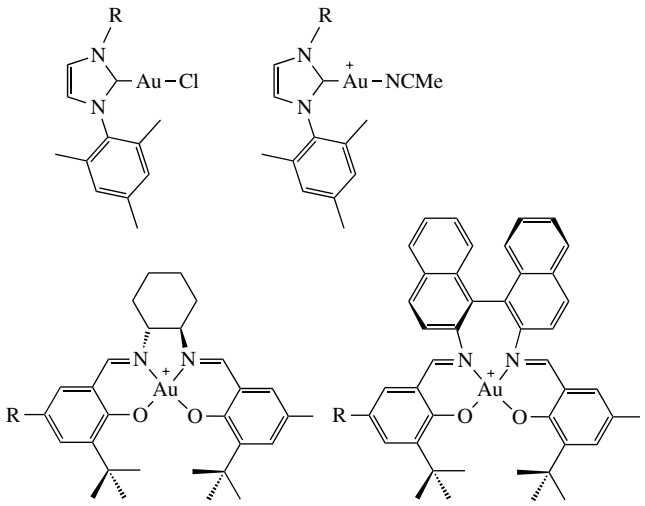


Scheme 6 Catalytic hydrothiolation of alkenes.

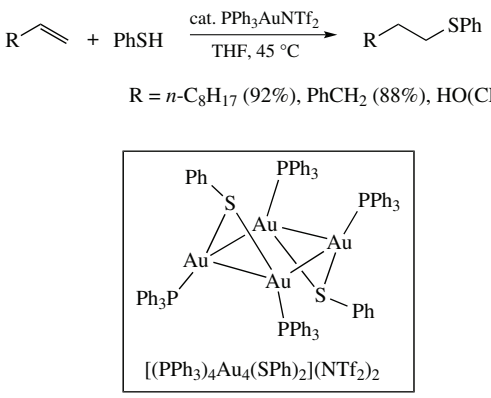
substituted alkenes can undergo catalytic hydrothiolation regioselectively. For example, Ogawa reported the Pd-catalyzed hydrothiolation of alkenes bonded directly to heteroatoms, such as vinyl ethers and vinyl lactams, to afford Markovnikov adducts regioselectively [Scheme 6(*b*)].[40] Hull reported a regiodivergent Rh-catalyzed hydrothiolation of allyl amines and imines. In this reaction, the use of bidentate phosphine ligands with larger natural bite angles ($\beta_n \geqslant 99°$) promotes a Markovnikov selective hydrothiolation, whereas smaller bite angles ($\beta_n \leqslant 86°$) lead to anti-Markovnikov selective hydrothiolation [Scheme 6(*c*)].[41] Gunnoe prepared a series of monomeric (NHC)Cu(SR) complexes, which catalyzed the addition of S–H bonds across electron-deficient alkenes to regioselectively deliver anti-Markovnikov products [Scheme 6(*d*)].[42] Hreczycho investigated scandium(III) triflate, Sc(OTf)$_3$-catalyzed regioselective-hydrothiolation of alkenes bearing silyl, hydroxyl and other heteroatom groups, to provide anti-Markovnikov adducts in good yields [Scheme 6(*e*)].[43,44]

Iglesias and Sánchez found that several gold–NHC complexes exhibited catalytic activity toward hydrothiolation of electron-deficient alkenes, proceeding with excellent anti-Markovnikov selectivity (Scheme 7).[45] Zhang conducted a theoretical study of gold(I)-catalyzed hydrothiolation.[46] Furthermore, Ogawa found that anti-Markovnikov selective hydrothiolation of unactivated alkenes with arene- or alkanethiols was attainable with a gold catalyst, such as PPh$_3$AuNTf$_2$ (Scheme 8);[47] this method was applied to the hydrothiolation of alkenes with methanethiol.[48]

Fleischer disclosed a protocol for the palladium-catalyzed tandem isomerization/hydrothiolation of allylarenes, which furnished benzylic thioethers [Scheme 9(*a*)].[49] Zhu developed a method for the nickel-catalyzed selective migratory hydrothiolation of alkenylarenes with thiols [Scheme 9(*b*)].[50]



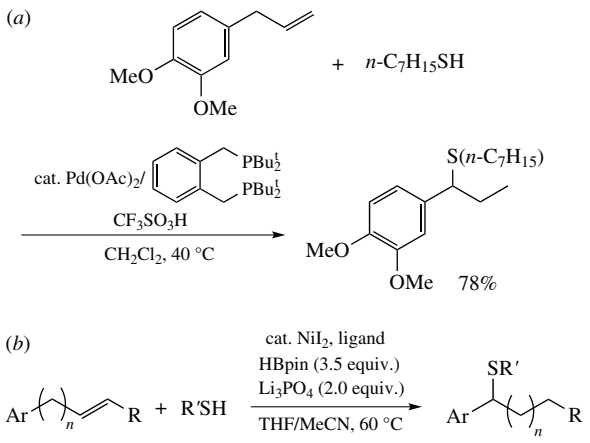
Scheme 7 Au–NHC complexes with high catalytic abilities toward hydrothiolation of electron-deficient alkenes.



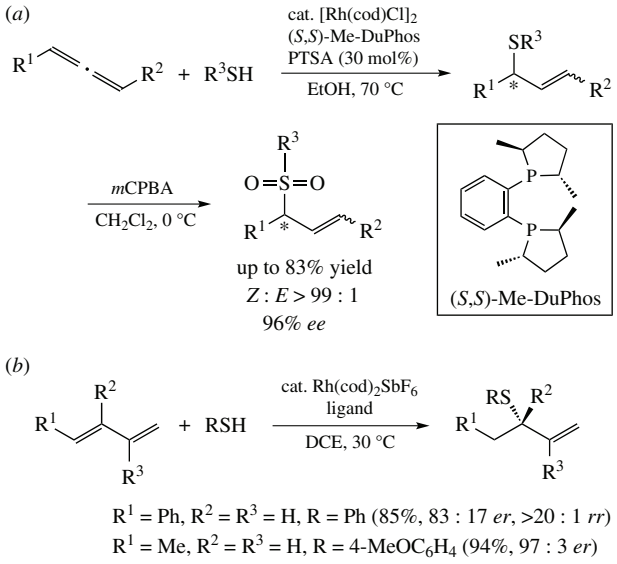
Scheme 8 PPh_3AuNTf_2-catalyzed anti-Markovnikov hydrothiolation of unactivated alkenes.

Recently, asymmetric hydrothiolations of substituted allenes[51] and conjugated dienes[52,53] have been reported, as shown in Scheme 10.

Catalytic bisthiolation of alkynes is another synthetically significant transformation. Ananikov and Beletskaya reported remarkable ligand effects for Ni- and Pd-catalyzed bisthiolation of alkynes.[54] Wu and Jiang developed a novel protocol for alkyne bisthiolation *via* a Pd-catalyzed three-component cascade reaction consisting of an alkyne, a diaryliodonium salt, and K_2S [Scheme 11(*a*)].[55] Kuniyasu *et al*. described the Pt-catalyzed



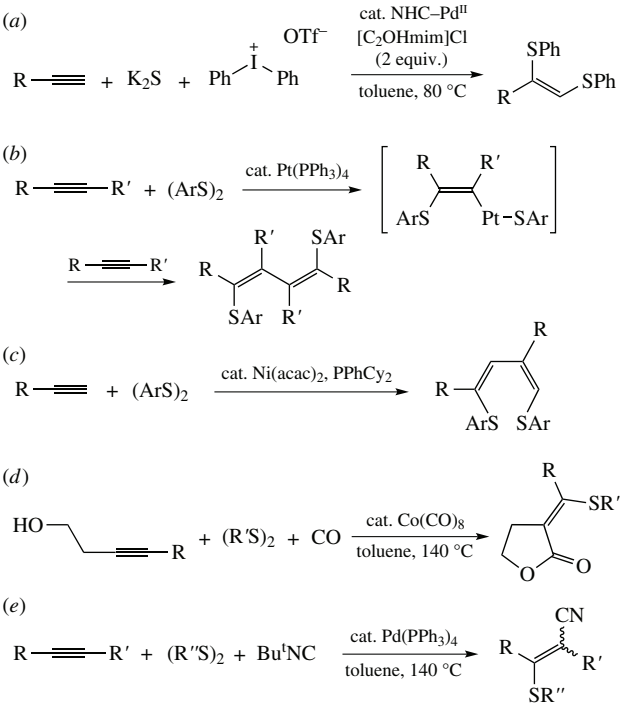
Scheme 9 Transition-metal-catalyzed tandem isomerization/hydrothiolation.



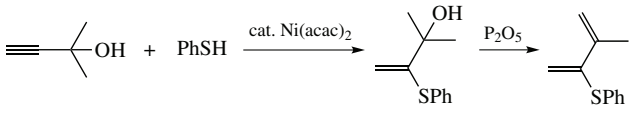
Scheme 10 Asymmetric hydrothiolation of substituted allenes and conjugated dienes.

dimerization–bisthiolation of alkynes for the synthesis of bisthiolated dienes [Scheme 11(*b*)].[56,57] Ananikov *et al*. reported nickel-catalyzed reaction of alkynes with diaryl disulfides provided an easy and convenient route to bisthiolated unsymmetrical 1,3-dienes [Scheme 11(*c*)].[58,59] Ogawa reported the Co-catalyzed carbonylative bisthiolation of alkynes and applied it to the synthesis of thiolated lactone derivatives [Scheme 11(*d*)].[60–62] When *tert*-butylisocyanide, an isoelectronic structure of CO, was employed instead of CO, Pd-catalyzed cyanothiolation of alkynes occurred [Scheme 11(*e*)].[63]

Ananikov recently reported eco-friendly synthesis comprising hydrothiolation of alkynes followed by elimination of water based on green metrics (Scheme 12).[64] Considering the environmental factor, recyclability of solvent, mass of solvent and starting materials, purification process, *etc*., the use of



Scheme 11 Further transformation toward various scaffolds based on the reactivity of thiolated species.

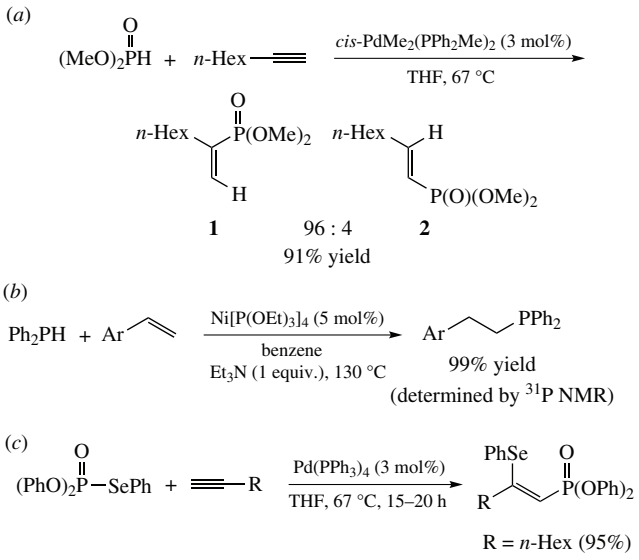


Scheme 12 Eco-friendly process of hydrothiolation of alkynes followed by elimination of water.

$Ni(acac)_2$ catalyst was more environmental. In the future, high atom economy methods will be developed that take into account not only the reaction yield but also the entire process.

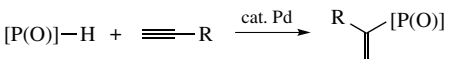
Atom-economic phosphination and phosphorylation *via* catalytic addition reactions

The role of organophosphorus compounds in organic synthesis, catalysis, materials chemistry, medicinal chemistry, and coordination chemistry becomes more significant each year.[65] Therefore, the development of synthetic methodologies for the production of organophosphorus compounds is a necessary endeavor, with increasing attention being paid to environmentally friendly methods. The addition of organophosphorus compounds comprising [***P***]–H bonds ([***P***]–H = R_2PH: secondary phosphine, $R_2P(O)H$: secondary phosphine oxide, $(RO)_2P(O)H$: *H*-phosphonates) to carbon–carbon unsaturated bonds is classified as an atom economical synthesis.[1,3,66] Reactions utilizing $(RO)_2P(O)H$ have been performed for decades, but they have been limited to ionic and radical processes.[67] Furthermore, the scope regarding the unsaturated bond reaction component was likewise limited. It is important to note that generally, the reactivity of these types of reactions varies greatly depending on the type of [***P***]–H.[68] The addition of [***P***]–H to unsaturated bonds using a metal catalyst had not been reported until the 1990s, as organophosphorus compounds have been regarded as catalyst poisons, due to their capacity for high coordination numbers. In 1996, Han and Tanaka announced the first Pd-catalyzed addition of $(RO)_2P(O)H$ to carbon–carbon unsaturated bonds [Scheme 13(*a*)].[69] Since this report, numerous addition reactions to unsaturated bonds using transition metal catalysts have been described. For example, in 2002, Beletskaya *et al*. published the first example of an intermolecular hydrophosphination of styrenes, catalyzed by Ni and Pd complexes [Scheme 13(*b*)].[70] Additionally, in 1996, Han and Tanaka described the first metal-catalyzed bisfunctionalization reaction involving the addition of a phosphoryl group to carbon–carbon unsaturated bonds. Namely, the Pd-catalyzed selenophosphorylation of terminal alkynes with $PhSeP(O)(OPh)_2$ affords the corresponding 1-(diphenoxyphosphinyl)-2-(phenylseleno)alkenes in good yields with excellent regio- and stereoselectivities [Scheme 13(*c*)].[71] Moreover, in the current decade, methods for obtaining various phosphorus compounds, such as benzophosphole oxide, *via* metal-catalyzed (photocatalyst *etc*.) cyclizations, under radical conditions, have been reported. This chapter focuses on recent catalytic addition reactions of phosphorus compounds including cyclizations and bis-functionalization.



Scheme 13 Breakthrough reactions in phosphination and phosphorylation using metal catalyst.

Recently, Han *et al*. elucidated the generality, scope, limitations, and mechanism of the palladium-catalyzed hydrophosphorylation of alkynes with P(O)–H compounds.[72] P(O)–H compounds can be classed into the following four types: $(RO)_2P(O)H$, $R(RO)P(O)H$ – *H*-phosphinates, $R_2P(O)H$ and H_3PO_2 – hypophosphinic acid; they can be used as starting materials for the desired Pd-catalyzed hydrophosphorylation, to produce the corresponding Markovnikov adducts in high yields. Appropriate selection of catalysts/ligands is critical for successful hydrophosphorylation. In the case of $(RO)_2P(O)H$, the ideal catalyst for the hydrophosphorylation is Pd/dppp, whilst $R(RO)P(O)H$ and $R_2P(O)H$ give optimal results with Pd/dppe/$Ph_2P(O)OH$. Reactions involving H_3PO_2 utilize $Pd(PPh_3)_4$ as the catalyst (Scheme 14).



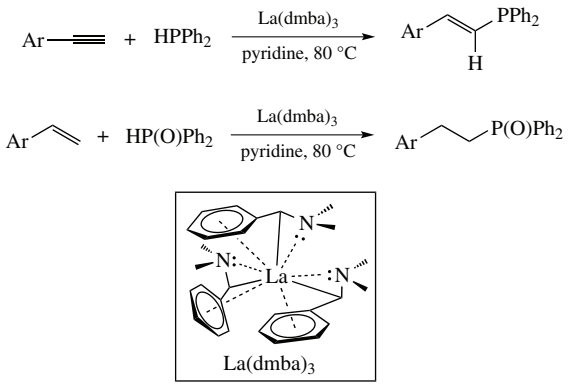
[P(O)]–H	Preferred catalyst
$(R'O)_2P(O)H$	Pd/dppp
$(R'O)R''P(O)H$	Pd/dppp/$Ph_2P(O)OH$
$R'R''P(O)H$	Pd/dppp/$Ph_2P(O)OH$
$(HO)P(O)H_2$	$Pd(PPh_3)_4$

Scheme 14 Preferred catalysts for the Pd-catalyzed hydrophosphorylation of alkynes.

On the other hand, hydrogen phosphoryl compounds bearing a free OH group (with the exception of H_3PO_2), *i.e*., phosphonic acid and phosphinic acids, were not suitable for the reaction, yielding no addition products under similar conditions.

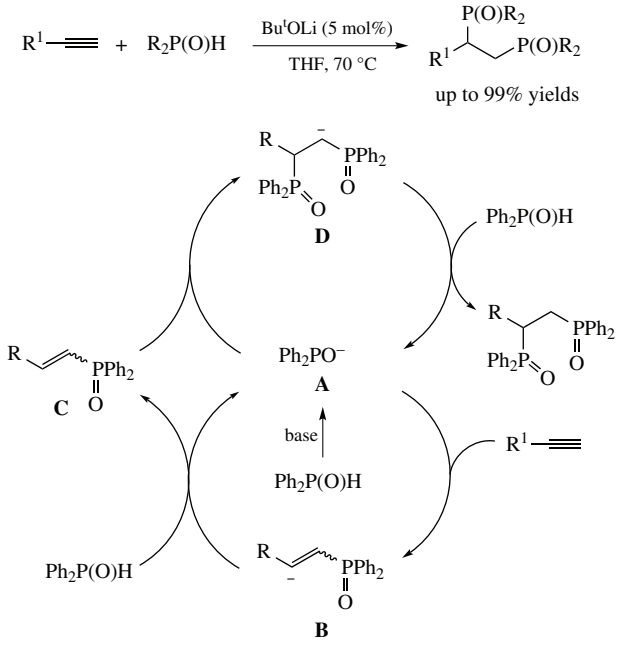
A pioneer study on the catalytic addition of [***P***]–H, employing lanthanoid metals is the report of Takaki *et al*., published in 2003.[73] They demonstrated the hydrophosphination of alkynes with diphenylphosphine (Ph_2PH), catalyzed by a Yb complex, [Yb(η^2-Ph_2CNPh)$(hmpa)_3$], which gave rise to alkenylphosphines and phosphine oxides in good yields, following an oxidative workup. Recently, Schmidt *et al*. developed lanthanum-catalyzed hydrophosphination and hydrophosphinylation procedures.[74,75] In the case of hydrophosphination, the catalyst, a lanthanum-based *N*,*N*-dimethylbenzylamine complex, induced mono-addition with high regioselectivity, yielding exclusively the anti-Markovnikov product stereoselectively (Scheme 15, top). The same complex also induced hydrophosphinylation of aromatic alkenes with a secondary phosphine oxide [$R_2P(O)H$], giving anti-Markovnikov products in good yields. (Scheme 15, bottom). A lanthanum-based *N*,*N*-dimethylbenzylamine complex acts as a precatalyst.

Double addition of $Ph_2P(O)H$ to alkynes yields bisphosphinyl compounds.[76] They can be easily reduced to the corresponding trivalent bisphosphino derivatives, which are useful as bidentate ligands of transition metal catalysts. Recently, Han *et al*. developed a base-catalyzed double addition of $R_2P(O)H$ to alkynes, whereby in the presence of a catalytic amount of Bu^tOLi, the addition of various H-phosphine oxides [$R_2P(O)H$)] to aromatic and aliphatic alkynes occurred efficiently, to give the corresponding bisphosphoryl compounds in excellent yields.[77]



Scheme 15 Lantanum-catalyzed anti-Markovnikov hydrophosphination and hydrophosphinylation.

The authors propose a reaction pathway as shown in Scheme 16. The base deprotonates $Ph_2P(O)H$ to generate a phosphoryl anion **A**, which reacts with an alkyne to generate the vinyl anion **B**. Subsequent protonation of **B** gives **C**, which reacts with **A** to deliver the desired bisphosphoryl product *via* anion **D**. Once **A** is generated, the catalytic cycle can remain active.

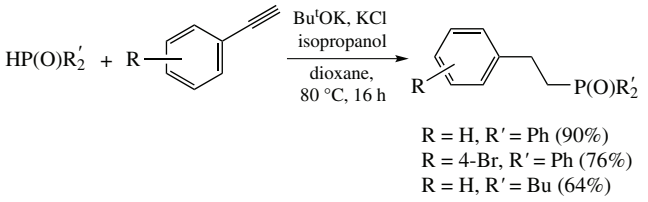


Scheme 16 Base-catalyzed double addition of $R_2P(O)H$ to alkynes and its proposed pathways.

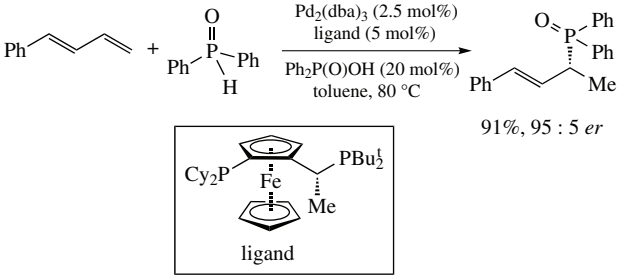
Chen, Han *et al*. reported an interesting reductive addition of $R_2P(O)H$ to alkynes.[78] In the presence of a catalytic amount of Bu^tOK, a mixture of a terminal alkyne, $R_2P(O)H$, isopropanol, and KCl in dioxane was heated and the corresponding β-arylphosphine oxide was obtained in good yield (Scheme 17). The authors propose that the hydrogen source for this reductive phosphinylation is derived from isopropanol.

Although numerous addition reactions of [***P***]–H have been reported to date, no enantioselective examples existed until 2018, when Dong *et al*. reported the first enantioselective phosphinylation (Scheme 18).[79] The ferrocene-based chiral bisphosphine ligand (shown in Scheme 18) controlled the Pd-catalyzed hydrophosphinylation of 1,3-dienes, to afford chiral allylic phosphine oxide.

Panda *et al*. reported an addition reaction of $Ph_2P(O)H$ onto a carbon–nitrogen triple bond, *i.e*., nitrile (Scheme 19).[80] When a

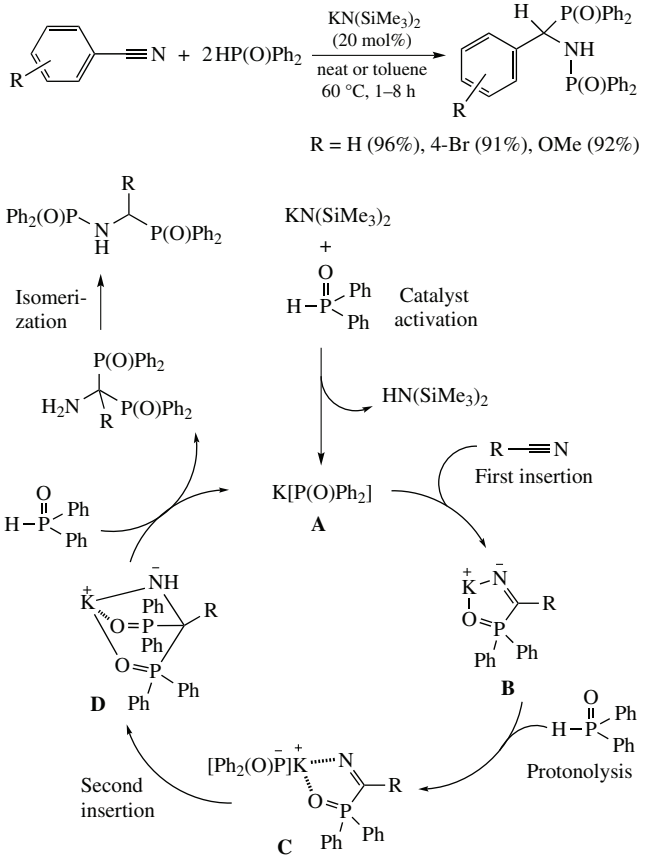


Scheme 17 Bu^tOK-mediated reductive addition of $R_2P(O)H$ to terminal alkynes.

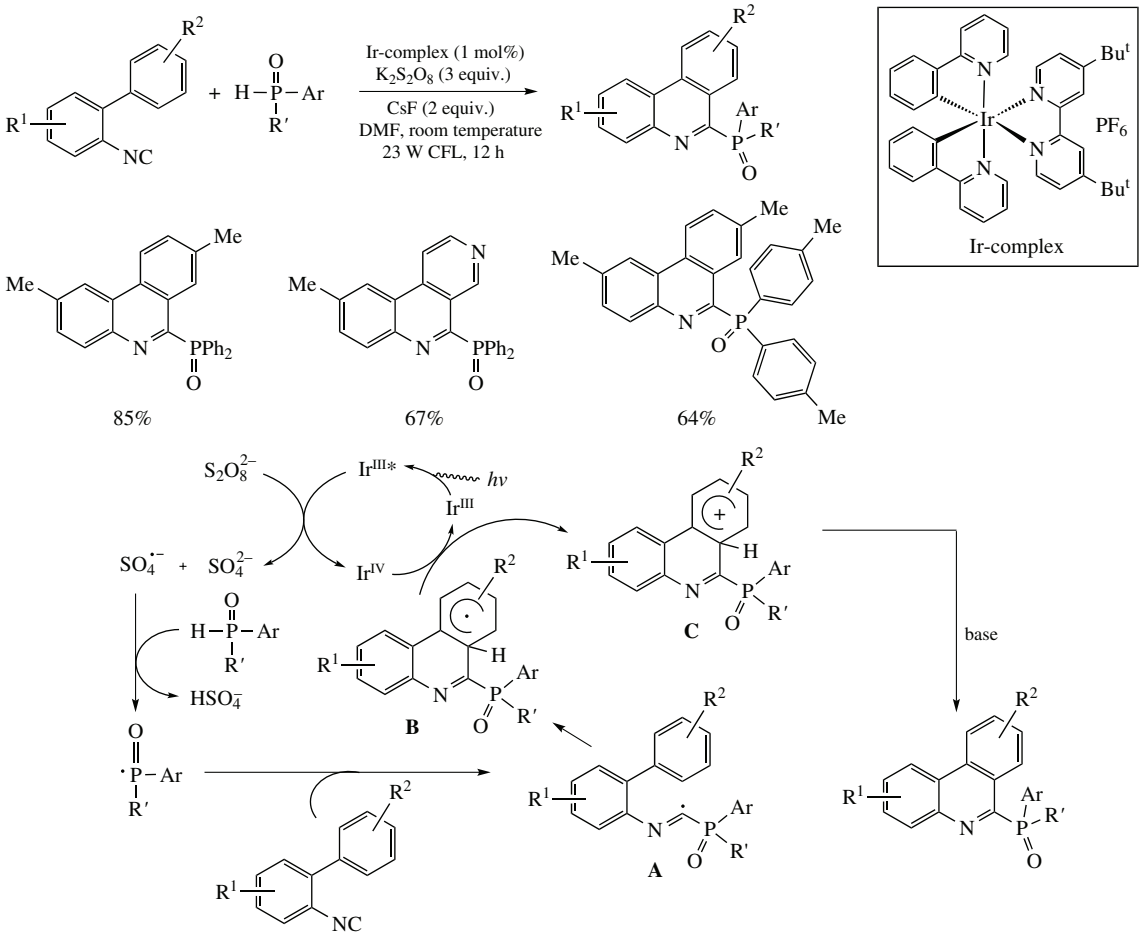


Scheme 18 The first enantioselective phosphinylation.

mixture of a catalytic amount of $KN(SiMe_3)_2$, aryl nitrile, and $Ph_2P(O)H$ in toluene, or neat, was heated at 60 °C, *N*-[(diphenylphosphoryl)(aryl)methyl]-*P*,*P*-diphenylphosphinic amide [$ArCHP(O)–Ph_2NHP(O)Ph_2$] was obtained in excellent yield. This reaction is useful for creating P–C–N–P motifs. The authors describe a plausible mechanism for the double hydrophosphorylation of nitriles, as shown in Scheme 19. In the first step, $KN(SiMe_3)_2$ reacts with diphenylphosphine oxide to give potassium diphenylphosphinite $KP(O)Ph_2$ (**A**) *via* the removal of $HN(SiMe_3)_2$ and **A** acts as the catalytically active species. In the next step, **A** adds to the C≡N triple bond, yielding potassium



Scheme 19 $KN(SiMe_3)_2$ catalyzed double hydrophosphorylation of nitriles and its proposed pathway.



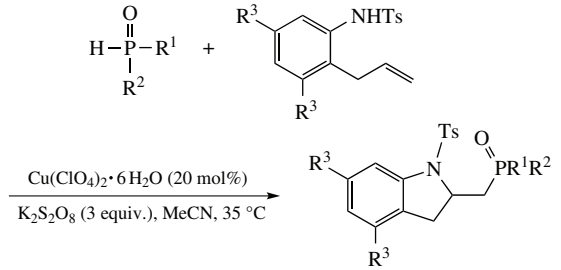
Scheme 20 Ir-catalyzed cascade reaction of biarylisocyanids with $Ph_2P(O)H$ and its plausible mechanism.

iminate complex **B**, which can be stabilized by delocalizing its positive charge into the phenyl groups of the nitrile and alkyne. Further reaction with $[HP(O)Ph_2]$ yields the five-membered doubly phosphorylated species **C**, which undergoes rearrangement and a second nucleophilic attack on the iminate carbon to give species **D**. In the final step, a third molecule of $[HP(O)Ph_2]$ undergoes protonolysis to produce the 1,1-regioisomer, which further isomerizes, itself yielding the corresponding 1,2-regioisomer product while regenerating the active metal catalyst.

Catalytic cyclizations generated by addition reactions, are likewise considered atom-economic reactions. Therefore, we will discuss the catalytic addition of [***P***]–H to carbon–carbon unsaturated bonds, involving a cyclization step under radical conditions. Reports on radical additions of [***P***]–H to carbon–carbon unsaturated bonds are numerous.[81–87] In 2014, Studer *et al*. disclosed the AgOAc-mediated radical cascade reaction for the construction of 6-phosphorylated phenanthridines.[88] Since then, a number of catalytic radical cyclization reactions have been studied.[89–92] Yan and Lu *et al*. reported the Ir-catalyzed cascade reaction of biarylisocyanides with $Ph_2P(O)H$.[93,94] This reaction delivers 6-phosphorylated phenanthridines *via* radical cyclization, when 1 mol% of complex $Ir(ppy)_2(dtbpy)PF_6$ was employed as the photocatalyst, and $K_2S_2O_8$ as the oxidant, under visible light irradiation (Scheme 20). The authors propose a reaction mechanism, as shown in Scheme 20. The photocatalyst Ir^{III}-complex is activated by visible light irradiation to form the excited-state, Ir^{III}-complex*, which then reduces the persulfate anion to produce an Ir^{IV}-complex, a sulfate anion, and a sulfate radical anion. The P-centered phosphinyl radical is generated through a hydrogen-atom-transfer (HAT) process, and subsequently undergoes addition with a biarylisocyanide, to form the radical intermediate **A**. Subsequent cyclization of **A** produces cyclohexadienyl-type radical **B**, which can be oxidized by the Ir^{IV}-complex to regenerate the Ir^{III}-complex and produce the cation intermediate **C**. Finally, **C** undergoes deprotonation to afford 6-phosphorylated phenanthridine.

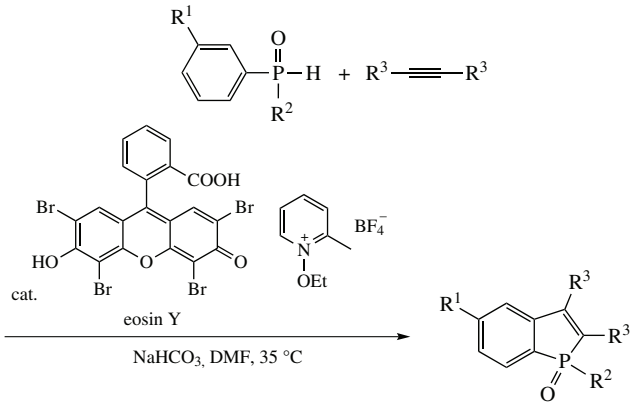
Yang *et al*. developed a copper-catalyzed cyclization for the synthesis of phosphorylated indolines.[95] When $Cu(ClO_4)_2{\cdot}6H_2O$ was employed as the catalyst and $K_2S_2O_8$ as the oxidant, the cyclization reaction of *N*-tosyl-2-allylanilines and $Ph_2P(O)H$ delivered the corresponding phosphorylated indolines (Scheme 21). The formation of a phosphoryl radical is a key step in the cyclization.

Lakhdar *et al*. demonstrated the synthesis of benzo[*b*]-phosphole oxides from reactions of arylphosphine oxides with



$R^1 = R^2 = Ph$, $R^3 = H$ (74%)
$R^1 = R^2 = 4\text{-}MeC_6H_4$, $R^3 = H$ (83%)
$R^1 = R^2 = Ph$, $R^3 = Me$ (64%)

Scheme 21 Copper-catalyzed cylization reaction of *N*-tosyl-2-allylanilines with $R_2P(O)H$.



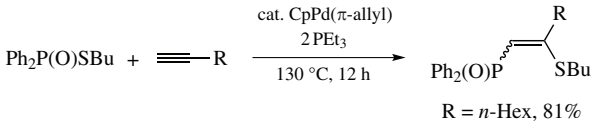
R^1 = H, R^2 = Ph, R^3 = 4-FC_6H_4 (77%)
R^1 = H, R^2 = Ph, R^3 = Pr (78%)
R^1 = H, R^2 = Bu^t, R^3 = Ph (72%)
R^1 = CF_3, R^2 = 4-$CF_3C_6H_4$, R^3 = Ph (69%)

Scheme 22 Photocatalyzed synthesis of benzo[*b*]phosphole oxides.

internal alkynes, under light irradiation, using eosin Y as the photocatalyst, and *N*-ethoxy-2-methylpyridinium tetrafluoroborate as the oxidant (Scheme 22).[96] Benzo[*b*]phosphole oxides have recently emerged as promising scaffolds for organic electronics and bioimaging probes.

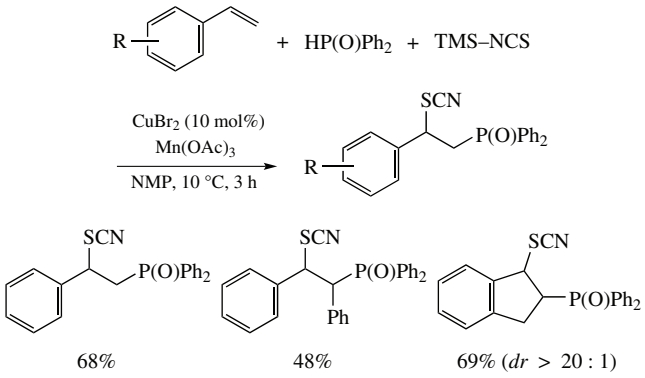
Bisfunctionalization of unsaturated bonds is an atom-economic reaction. Concerning bisfunctionalization with phosphorus groups, 1,2-addition reactions to unsaturated bonds of diphosphines have been known since the 1960s.[97–99] The majority of these reactions proceed under radical conditions. In recent years, bisfunctionalization to unsaturated bonds using characteristics of the phosphorus radical reaction have also been reported. On the other hand, as described above, the double phosphorylation by [***P***]–H onto alkynes is an example of an efficient bisfunctionalization. In 1996, Han, Tanaka *et al*. reported the first transition metal-catalyzed bisfunctionalization of unsaturated bonds. Specifically, it involved a Pd-catalyzed phosphorylselenation of alkynes with compounds possessing a P–Se bond.[71] Since this study, a number of catalyzed bisfunctionalization reactions have been reported.[100] Recent examples of catalyzed bisfunctionalization reactions are discussed below.

Following the discovery of the palladium-catalyzed addition of $(RO)_2P(O)SPh$ to alkynes,[100] the development of a metal-catalyzed addition of $Ph_2P(O)SPh$ to alkynes did not take place until much later. This is attributed to the difference in reactivity of the phosphoryl species $(RO)_2P(O)R$, and phosphine oxide species $R_2P(O)R$. In 2012, Tanaka *et al*. eventually discovered appropriate conditions for the regioselective Pd-catalyzed phosphinylthiolation of alkynes (Scheme 23).[101]



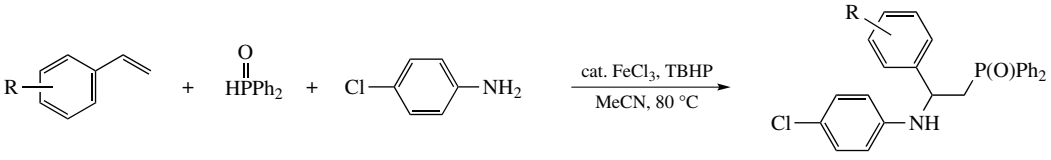
Scheme 23 Palladium-catalyzed phosphinylthiolation of terminal alkynes.

Concerning the simultaneous addition of P and S groups, Zou, Zhang *et al*. reported a Cu-catalyzed thiocyanophosphinylation of alkenes (Scheme 24).[102] The authors rationalized that this reaction proceeded *via* a phosphinyl radical process, generated from the oxidation of $Ph_2P(O)H$ with $Mn(OAc)_3$. This simultaneous addition gives regioselective adducts in good yields.

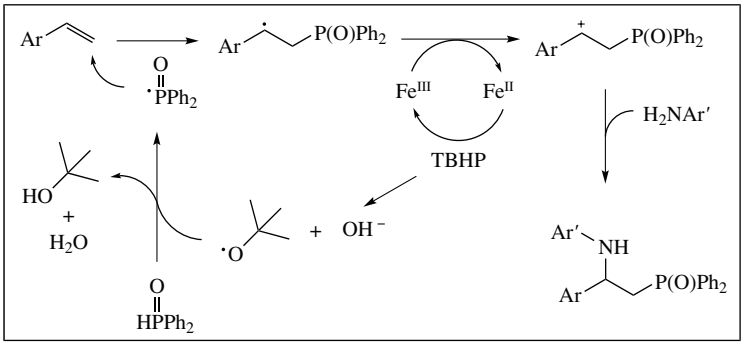


Scheme 24 Cu-catalyzed thiocyanophosphinylation of alkenes.

Wang, Fang *et al*. accomplished the Fe-catalyzed bisfunctionalization of styrenes with $Ph_2P(O)H$ and anilines (Scheme 25).[103] In the reaction, α,β-aminophosphinoylation products were efficiently obtained. The reaction mechanism is shown in Scheme 25; the initial reaction of $Ph_2P(O)H$ with TBHP



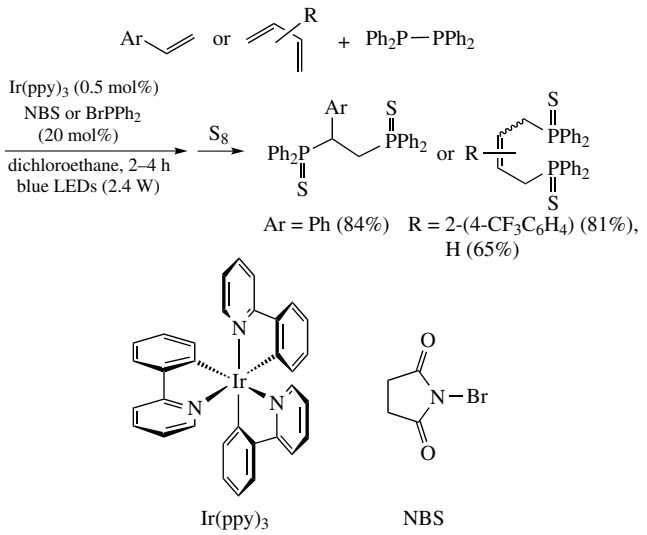
R = H (80%), 4-Bu^t (85%), 4-Cl (73%)



Scheme 25 Fe-catalyzed phosphinylamination of styrenes with $Ph_2P(O)H$ and anilines.

(*tert*-butyl hydroperoxide) provides the phosphinoyl radical, which effects an addition to styrene, to afford the alkyl radical intermediate. The carbonation intermediate is generated through a SET process with an Fe^{III} catalyst. Finally, nucleophilic trapping by the amine affords the corresponding α,β-aminophosphinoylation products.

Hirano, Miura *et al*. detailed the Ir-catalyzed bisfunctionalization of two phosphine groups.[104,105] Bisphosphination occurred when a mixture of diphosphine and a styrene or diene was irradiated using a blue LED, in the presence of catalytic amounts of $Ir(ppy)_3$ and NBS (*N*-bromosuccinimide). Following treatment with S_8, 1,2-bisthiophosphinylethane, or 1,4-bisthiophosphonylbut-2-ene were obtained in good yield, respectively (Scheme 26). Similarly, and in addition to the reaction of P–P,[106–110] bifunctionalization reactions of P–O,[111] P–S,[112,113] P–Cl,[114] P–Si,[115] P–Se[116] and P–Te[117] have been reported.



Scheme 26 Ir-catalyzed bisphosphination of alkenes and dienes with tetraphenyldiphosphine.

Conclusion

In this mini-review, recent catalytic addition reactions of organosulfur and organophosphorus compounds were described. The synthesis of organosulfur compounds relied on hydrothiolation, which could be controlled by precisely designed catalysts. As to the regioselectivity of hydrothiolation, Markovnikov addition seems to occur when the catalysts cause 'thiometalation' in the catalytic cycle. In sharp contrast, anti-Markovnikov hydrothiolation tends to proceed when the catalysts lead to 'hydrometalation'. Regarding the production of organophosphorus compounds, precisely controlled cyclization and regioselective bisfunctionalization have been reported. Considering the environmental impact factor (E-factor)[64] of these addition reactions, the hydrothiolation methods are generally more eco-friendly as compared with the hydrophosphorylation methods. However, the green metrics is still by no means satisfactory, and many more studies on hydrothiolations and hydrophosphorylations are required. The findings provided by the reports mentioned in this mini-review are fundamental and pertinent, paving the way for further discoveries and advancements in the field.

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