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Recent advances in the Carbon–Phosphorus (C–P) bond formation from unsaturated compounds by *s*- and *p*-block metals

Indrani Banerjee*[a][b] and Tarun K. Panda*[a]

Researchers around the globe have witnessed several breakthroughs in *s*- and *p*-block metal chemistry. Over the past few years, several applications in catalysis associated with these main group metals have been established, and owing to their abundance and low cost and they have proved to be essential alternatives to transition metal catalysts. In this minireview, we present a detailed discussion on the catalytic addition of P–H bonds from various phosphine reagents to multiple bonds of unsaturated substrates for the synthesis of organophosphorus compounds with C–P bonds promoted by various *s*- and *p*-block metal catalysts, as published in the last decade.

1. Introduction.

For the past several years, transition metals have been considered preeminent compounds in organic chemistry and have extensively been utilized in diverse catalytic methodologies. The variety of derivatives of transition metal catalysts has urged the evolution of several valuable reagents for critical reaction schemes, highly acknowledged in textbooks.[1] The field of organometallic chemistry has also witnessed progressive developments in the use of transition metal catalysts for the functionalization of several small molecules in past few years.[2-3] The existence of variable oxidation states, participation of valence *d*-electrons, variable spin states, and coordination modes are important features that allow for transition metals to be utilized in diverse ways in chemical transformations. Likewise, for synthetic chemists, rare-earth metal catalysts have also proved to be highly proficient in a variety of applications.[4] Despite their significant utility, there are concerns about transition metal and rare-earth metal precursors being expensive, scarce in terms of availability, and having generally toxic properties. Further, heavy metal deposition in the corresponding products also renders such metals unattractive for use in atom-economic processes.[5] In certain circumstances, transition metal catalysts demand co-catalysts and other additives for the efficiency of reaction protocols.[6] Thus, research in modern chemistry focuses on continuous growth in new strategies and utilities in catalysis; in particular, those that advance the use of non-toxic, comparatively cheap, and readily available earth-abundant metals considered to support greener approaches and thereby offering appealing aspects that address disadvantages from the use of precious and heavy metals.[7]

This greener approach can be aided by *s*- and *p*-block metals, which represent the most abundant elements in the earth's crust and possess diverse properties in the periodic table. Numerous recent discoveries have exhibited that the behavior of several main group compounds is similar to that of transition metal complexes.[8] These elements, due to their inexpensiveness and abundant availability, as well as environmentally benign nature, are highly useful for a range of applications.[9-11] Common features that led to the desire to synthesize stable main group compounds are: (i) multiple bond formation between heavier main group elements such as Al, Si, P;[12] (ii) stable low-valent elements with open coordination sites;[13] (iii) stable radical generation on the heavier main group elements;[14] (iv) stable singlet diradicaloid electron configurations.[15] An attractive property of *s*-block elements is their low oxidation state, which makes them highly effective in many catalytic applications; yet, their analysis and catalytic studies are underdeveloped.[16] The apparent neglect of these elements can be attributed to the following factors: lack of synthetic proficiency, high susceptibility to air and moisture, and short-lived reactivity. As a result, they have been limited to synthetic procedures performed in the laboratory, and require more detailed study. Regarding the atomic sizes and charges of the *s*- and *p*-block elements, the electropositive cations having Lewis acidity and bonded to respective nucleophilic anions lead to interactions of π-bonds of several unsaturated compounds, which is a prerequisite for several hydroelementation reactions.[17]

In recent years, catalysis has become a predominant tool for development in science and technology. In this context, catalytic methodologies for the addition of E–H (E = N, P, S, O, C, B, Si) bonds to various unsaturated multiple bonds serve as an atom-economic approach. Catalytic hydroelementation reactions are thus highly favoured by synthetic chemists and significant progress in research has been observed over the past few years.[18] Hydroamination,[19] hydroboration,[20] hydrothiolation,[21] hydrosilylation,[22] hydroalkoxylation,[21c,23] and so on represent important classes of reactions with the generation of ubiquitous organic compounds. Similarly, the addition of P–H bonds via catalytic protocols for achieving an abundance of organophosphorus compounds generating C–P bonds has also gained considerable recognition in research fields. Metal-catalyzed C–P bond formations through hydroelementation reactions involve typical electrophilic carbon moieties from unsaturated molecules along with nucleophilic organophosphorus substrates in a reaction scheme.

Indrani Banerjee has obtained her BSc in Chemistry from Dinabandhu Andrews College, Calcutta University in 2012, and her MSc from Pondicherry University in 2014. She has joined as a doctoral student in the Department of Chemistry at Indian Institute of Technology (IITH) India under the supervision of Prof. Tarun K. Panda in 2015 and she was awarded the degree in 2020. Dr. Banerjee has joined as Assistant Professor in the School of Basic and Applied Sciences at Raffles University, Rajasthan, India. Her research area involves catalytic applications promoted by earth-abundant and environment metal complexes.

Tarun K. Panda obtained his Master of Science in Chemistry from IIT, Kanpur in 2002 and received his Dr. rer. nat from Freie Universität Berlin, Germany in 2005 under the supervision of Prof. Dr. Peter W. Roesky in the area of organometallic chemistry. Dr. Panda joined the working group of Prof. Dr. Matthias Tamm at Technische Universität Braunschweig, Germany as a postdoctoral fellow in 2006. He was awarded the Japan Society for the Promotion of Science (JSPS) postdoctoral fellowship in 2008 to work with Prof. Kazushi Mashima in the Graduate School of Engineering, Osaka University, Japan. In 2010, he returned to India to join the Department of Chemistry, Indian Institute of Technology Hyderabad (IITH) India as Assistant Professor. He was promoted to Associate Professor in 2015 and since May 2019, he is holding the position of Professor at the same Institute. He has been awarded the CRSI bronze medal 2021 for his significant contribution to Chemistry. His principal research interests include the development of well-defined earth-abundant, non-toxic, and environmentally benign metal complexes using non-cyclopentadienyl based ligands and their exploitation in homogeneous catalysis under ambient reaction conditions.

1.1. Reactions involving typical organophosphorus substrates.

Organophosphorus compounds have a crucial role to play in major physiological processes of photosynthesis and energy transfer.[24] They are also part of extensive applications in several organic syntheses,[25] medicinal fields,[26] synthons for natural products,[27] and in organometallic chemistry as depicted in figure 1.[28] The variation in reaction schemes for the addition of P–H bonds across C≡C, C=C, C=O, and C=N unsaturated bonds is dependent on the number of oxygen atoms in the organophosphorus substrates.[29] The substrate HPR$_2$ with no oxygen atoms represents one category of hydrophosphination reactions that have been widely carried out by researchers. HP(O)R$_2$ with one oxygen atom refers to hydrophosphorylation reactions while hydrophosphinylation reactions involve HP(O)(OR)R' containing two oxygen atoms. The presence of three oxygen atoms in the HP(O)(OR)$_2$ substrate represents hydrophosphonylation.[30] The classification of these reaction schemes has been illustrated in figure 2.

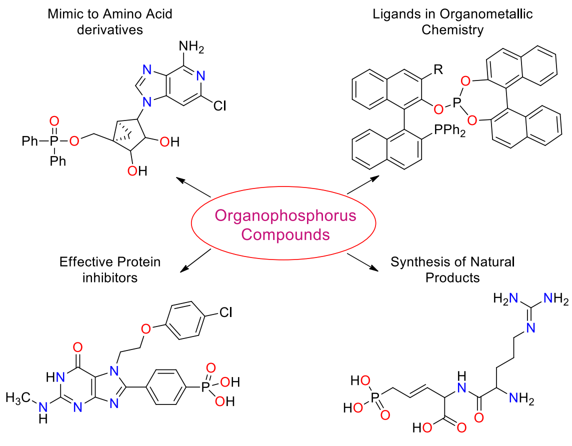


Figure 1. Applications of organophosphorus compounds.

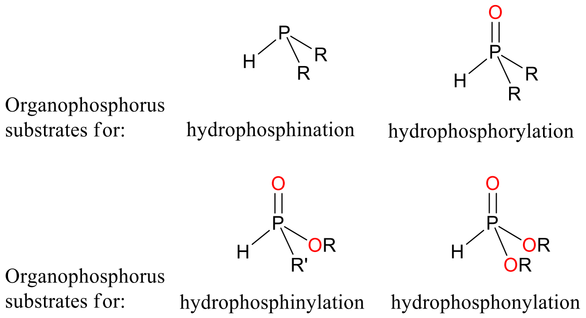


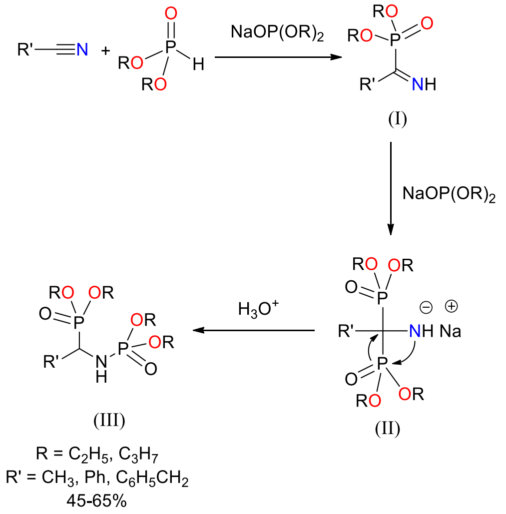
Figure 2. Classification of organophosphorus substrates.

Several metal catalysts across the periodic table have been employed in the enumerated reactions for the advancement of C–P bond formation. Numerous transition metals and rare earth metal catalysts have been proficiently utilized for significant hydrophosphination reactions as well as other classes of reactions.[29,31-43] The following section presents an overview of reaction strategies with a variety of *s*- and *p*-block metal catalysts for C–P bond formation via hydrophosphination, hydrophosphorylation, hydrophosphination and hydrophosphonylation from a variety of unsaturated compounds.

2. *s*- and *p*-block metals-mediated C–P bond formation from unsaturated compounds.

2.1. P–H bond addition to organic nitriles.

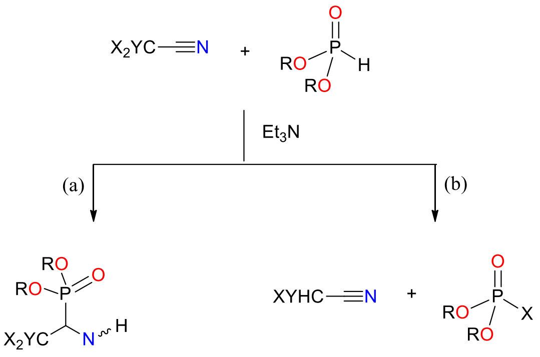
The *s*- and *p*-metal catalyzed reduction of the C≡N group have been confined yet, provoking considerable research for the development of potentially active catalysts. The initial report suggested the nitrile hydrophosphonylation was achieved with the use of dialkyl phosphites in the presence of sodium salts to acquire phoshorylamino phosphonates as the major product in moderate quantities up to 65%. The mechanism used was the addition of sodium dialkylphosphite to the nitrile C≡N group to provide the iminophosphonate intermediate I. The reaction proceeds with the addition of another molecule of sodium dialkylphosphite which further undergoes C,N-phosphoryl shift to achieve the final 1,2-regioisomer III (Scheme 1). However, neither monophosphoryl intermediate I nor iminophosphonates could be isolated from the described reaction mechanism.[44]



Scheme 1. The proposed mechanism for synthesis of sodium salt–mediated phoshorylamino phosphonates.

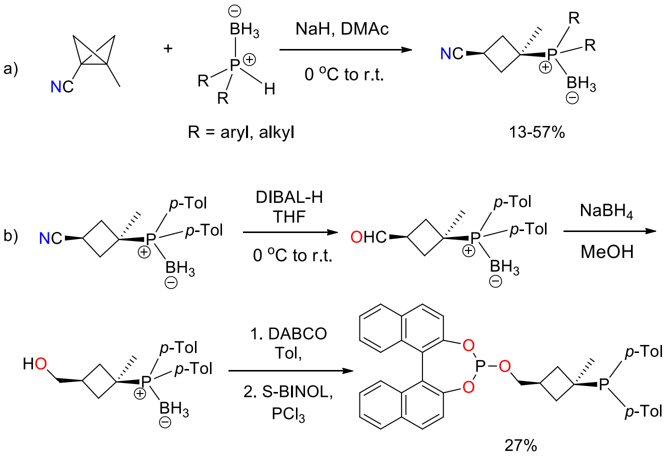
The first NH-imidoyl phosphonates were isolated in 2007 in good yields of 75-87% by the Onys'ko working group from the reaction between dialkylphosphites and trifluoroacetonitrile mediated by trimethylamine.[45a] The fully characterized NH-iminophosphonates proved to be valuable synthons for a range of fluorinated aminophosphonic compounds.[45] A similar base-promoted hydrophosphonylation was attempted with haloacetonitriles by the same research group. The reaction protocol of dialkylphosphites to trihaloacetonitriles catered two alternate pathways as illustrated in scheme 2.[46] Trifluoroacetonitriles provided iminophosphonates as displayed in route (a), which drastically tuned to route (b) forming dichloro-acetonitrile and the equivalent chlorophosphate on replacing the fluorine atoms in trifluoroacetonitrile with the chlorine atoms.

Later, in 2016, the hydrophosphination of bicyclo[1.1.0]butane-1-carbonitrile derivatives was first investigated with phosphine boranes. Unusual cyclobutylphosphine boranes were achieved as readily separable diastereomers, although with poor to moderate yields up to 57% (Scheme 3a). A high tolerance has been observed for bicyclobutane and phosphine groups with aryl and alkyl derivatives. Chiral bidentate phosphine-phosphite ligands were easily obtained by the conversion of nitrile functional groups to aldehydes and alcohols (Scheme 3b).[47]



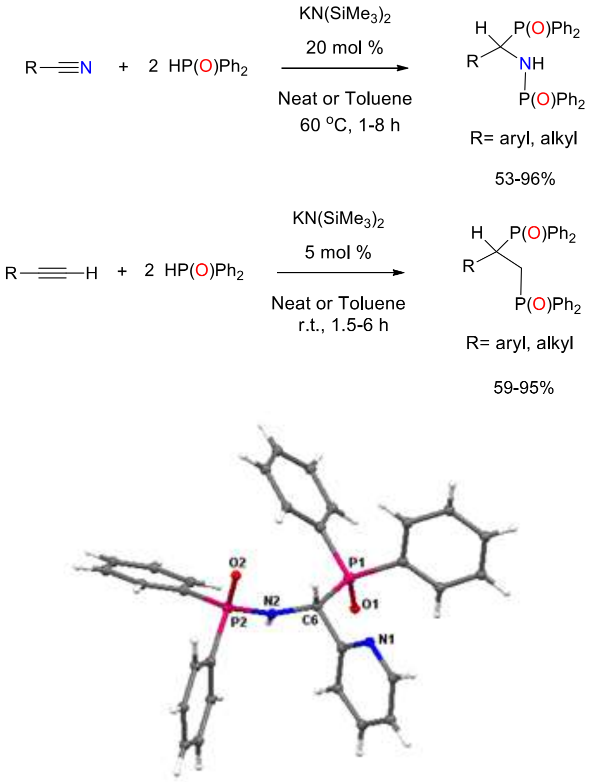
X	Y	a : b	
		R = Et	R = Ph
F	F	100:0	100:0
F	Cl	10:1	10:1
Cl	F	1:2	10:1
Cl	Cl	0:100	0:100

Scheme 2. Two alternative pathways for base-mediated hydrophosphonylation of haloacetonitriles.



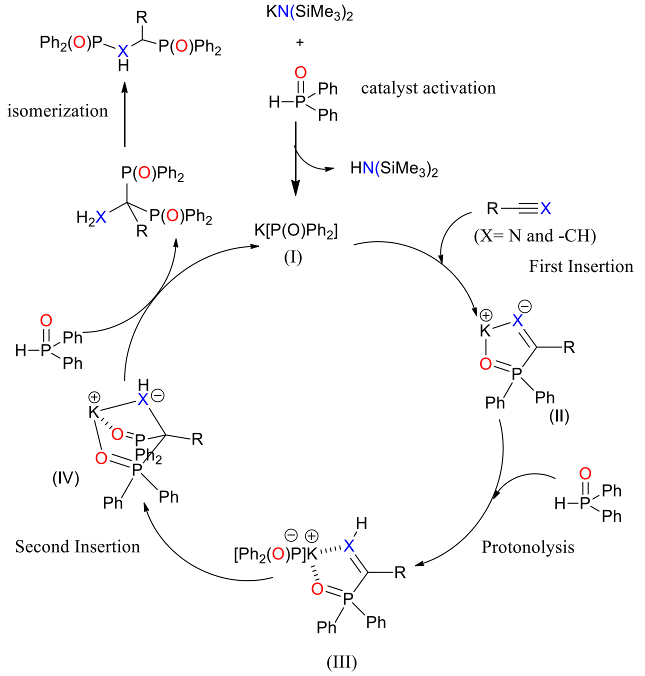
Scheme 3. (a) Hydrophosphination of bicyclo[1.1.0]butane-1-carbonitrile derivatives with phosphine boranes. (b) Synthesis of the chiral bidentate phosphine-phosphite ligand from cyclobutylphosphine boranes.

Very recently, Panda and coworkers investigated the double hydrophosphorylation of organic nitriles and alkynes using diphenylphosphine oxide promoted by alkali metal hexamethyldisilazides. Organophosphorus compounds bearing the P–C–N–P framework are very rare. The alkali metal-mediated hydrophosphorylation of nitriles and alkynes resulted in the formation of the 1,2-regioisomers acquiring the P–C–N–P and P–C–C–P linkages respectively with good to excellent yields up to 96%.[48] $KN(SiMe_3)_2$ was recognized as the proficient catalyst that carried out double hydrophosphorylation of nitriles and alkynes under ambient and neat condition (Scheme 4). A double hydrophosphorylated product achieved from picolinitrile and diphenylphosphine oxide has also been presented in the reaction scheme.



Scheme 4. $KN(SiMe_3)_2$ promoted double hydrophosphorylation of nitriles and alkynes. The solid-state structure of double hydrophosphorylated product obtained from picolinonitrile and diphenylphosphine oxide. CCDC No. 1869184. See Ref. 48

Scheme 5 sets out a proposed mechanism associated with the generation of potassium diphenylphosphinite $[KP(O)Ph_2]$ (I) as the active catalyst. The addition of $[KP(O)Ph_2]$ to the -C≡N and -C≡CH triple bond takes place subsequently. The corresponding five-membered iminate or alkenyl intermediate (II) undergoes protonolysis by diphenylphosphine oxide molecules followed by rearrangement.

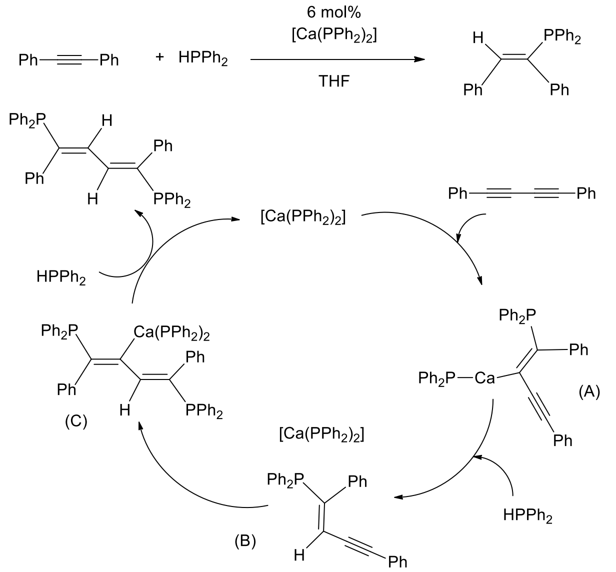


Scheme 5. The most plausible mechanism for alkali metal-mediated double hydrophosphorylation of nitriles and alkynes.

Protonolysis by the third molecule of $HP(O)Ph_2$ generates the five-membered doubly phosphorylated intermediate (III). Rearrangement followed by a second nucleophilic attack on the alkenyl/iminate carbon produces compound IV. The final addition of a third molecule of $[HP(O)Ph_2]$ affords a 1,1-addition product that further isomerizes to produce the 1,2-regioisomer. However, *p*-block metal catalysts have not been observed to make significant P–H bond additions to the nitrile substrates and are thus a significant area for development.

2.2. P–H bond addition to alkynes.

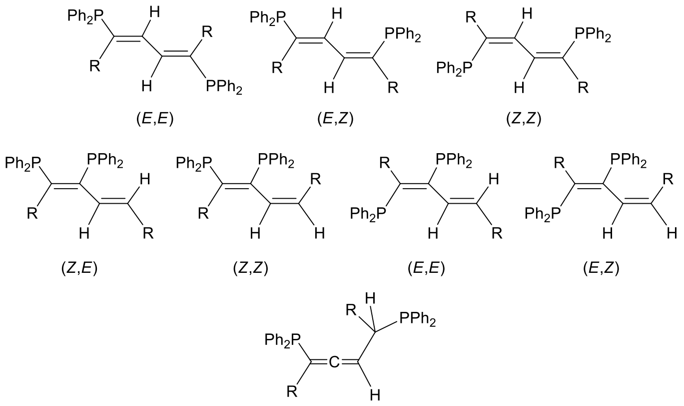
The hydrofunctionalization of the C≡C group has also been an emerging field in the study of catalysis. Calcium bis(diphenylphosphanides), being an eminently competent catalyst, was initially employed by the Westerhausen research group as an alternative to transition metal catalysts for hydrophosphination reactions. The use of 6 mol% $[(THF)_4Ca(PPh_2)_2]$ in the hydrophosphination of diphenylacetylene resulted in the formation of the *cis*-addition product, *trans*-1,2-diphenyl-1-diphenylphosphanylethene in quantitative yields (Scheme 6).[49] The catalytic reduction of diphenylbutadiyne also efficiently proceeded to achieve 1,4-diphenyl-1,4-bis(diphenylphosphanyl)-buta-1,3-diene by the reaction methodology. The proposed mechanism has been shown in scheme 6 that suggests the $[Ca(PPh_2)_2]$ addition to diphenylbutadiyne forming complex **A**. The reaction complex **A** with $HPPh_2$ followed by rearrangement affords the final product.



Scheme 6. Ca(II)-mediated hydrophosphination of diphenylacetylene. The catalytic cycle of hydrophosphination of diphenylbutadiyne.

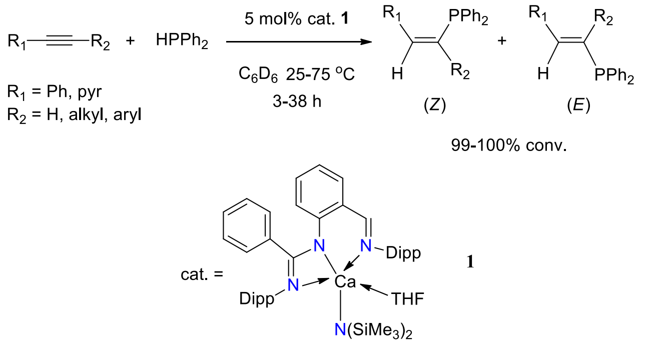
A solvent-free and catalyst-free methodology for the synthesis of *α*-aminophosphonates was achieved. Although the three-component reaction between isoquinoline or benzothiazole with activated acetylenes and diphenylphosphonate afforded the desired aminophosphonates in room temperature and a short reaction time with high yields (60-90%), a relatively broad substrate scope was a limitation of the strategy.[50] This led to the development of active catalyst systems for improved reaction strategies.

The Westerhausen group continued their research with [Ca(PPh$_2$)$_2$] and documented heterofunctionalization of a broader scope of alkynes and butadienes, yielding 76-95% of the corresponding hydrophosphinated products were achieved.[51] Hydrophosphination of butadienes generated a class of isomers of vinylphosphanes. The sort of substituents of the butadiyene and their steric factor afforded a series of constitutional isomers as set out in scheme 7.



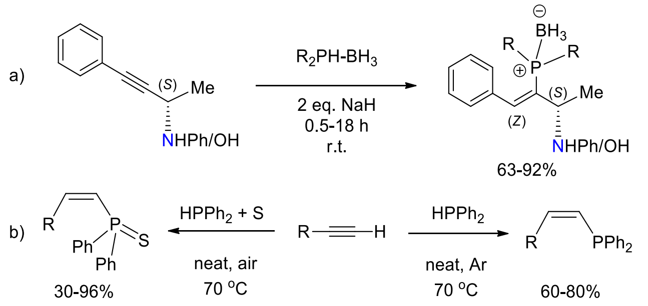
Scheme 7. Ca(II)-mediated hydrophosphination of a variety of diphenylbutadiyne affording a library of isomers of hydrophosphalated buatdienes.

A year later, Cui and workers reported the use of calcium complex **1** supported by the tridentate imino-amidinate ligand as an effective catalyst for the intermolecular hydrophosphination of hindered alkenes and alkynes.[52] Catalyst **1** was synthesized in 78% yield as a light-yellow solid by the reaction between the ligand [2-{NHC(Ph)NAr}C$_6$H$_4$CHNAr] and calcium diamide [Ca{N(SiMe$_3$)$_2$}-(THF)$_2$]. The intermolecular hydrophosphination of terminal alkynes and internal alkynes produced a mixture of *syn*- and *anti*-addition products. Catalyst **1** was recognized to afford *Z*-isomer preferably over *E*-isomer with complete conversion as displayed in scheme 8.

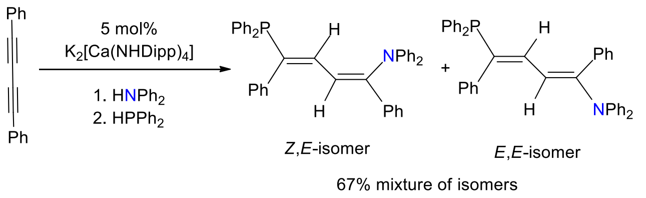


Scheme 8. Ca(II) complex-mediated hydrophosphination of terminal and internal alkynes.

Several catalyst-free protocols for the addition of P–H bonds to unsaturated C≡C moieties have gained recognition in the past few years. Catalyst-free hydrophosphination of propargylic amines and alcohols with phosphineboranes was first established in 2013 (Scheme 9a).[53] The reaction was carried out smoothly in the presence of DMAc as a solvent along with 2 eq. of NaH, which provided the desired phosphineborane amines and alcohols as diastereomeric *P*-chiral products in good yields. The protecting groups or pyrophoric secondary phosphines did not need to be used and was a major convenience of this reaction protocol. Additionally, alkyne hydrophosphination and hydrothiophosphination with a wide substrate scope, completed under solvent-free and catalyst-free conditions to achieve moderate to good yields of alkenylphosphines and alkenylphosphine sulfides (Scheme 9b), have been reported.[54]

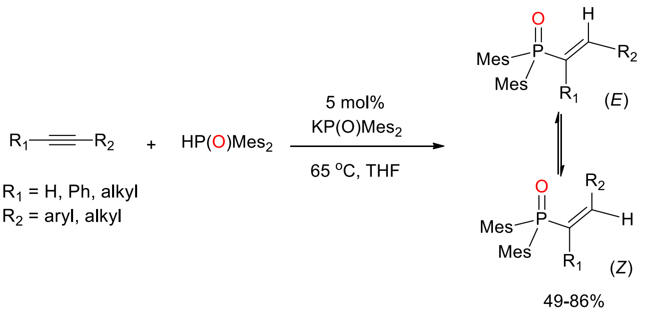


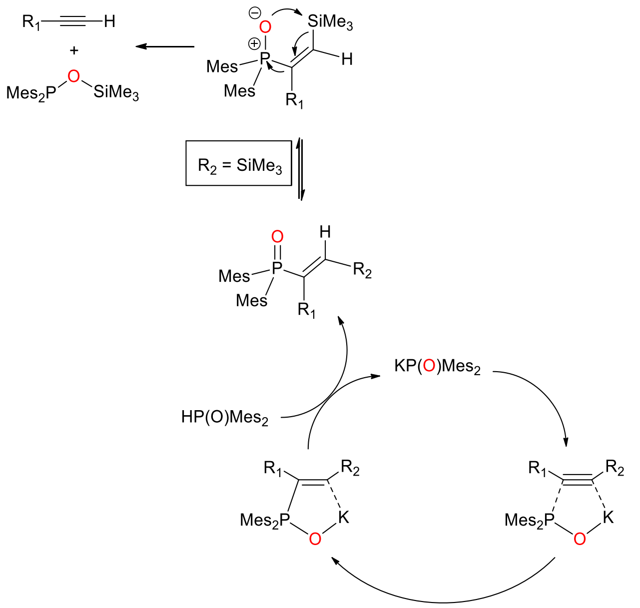
Scheme 9. (a) catalyst-free hydrophosphination of propargylic amines and alcohols with phosphine-boranes. (b) catalyst-free alkyne hydrophosphination and hydrothiophosphination.



Scheme 10. Caliate $K_2[Ca(NHDipp)_4]$ mediated hydropentelation of diphenylbutadiyene.

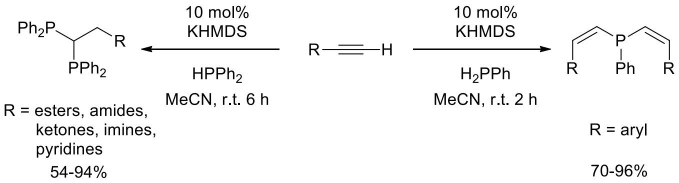
Westerhausen and his team had earlier provided a benchmark in P–H bond additions through simple and efficient reaction strategies.[49,51] They continued their research and introduced an improved catalyst $K_2[Ca(NHDipp)_4]$ that presented high catalytic activity toward the hydropentelation reaction on diphenylbutadiyene.[55] The coligand-free calcium metal catalyst is easily synthesized and shows reactivity toward a two-step and one-step synthesis of 1-Diphenyamino-1,4-diphenyl-4-(diphenylphosphanyl)buta-1,3-diene providing *Z,E*- and *E,E*-isomers. Scheme 10 sets out the one step $K_2[Ca(NHDipp)_4]$ mediated hydroamination and hydrophosphanylation of diphenylbutadiyene. A proposed mechanism was documented for the two-step hydroamination and hydrophosphanylation reaction sequence. Additionally, the researchers also conducted intermolecular hydrophosphorylation reaction on a library of alkynes R^1-C≡C-R^2 (R^1 = H, alkyl, Ph; R^2 = alkyl, Ph, COOMe, $SiMe_3$, $Si(^iPr)_3$ mediated by potassium dimesitylphosphinite.[56] The E/Z isomers of the corresponding alkenyldimesitylphosphine oxides are entirely dependent on substitutional variations in the alkyne substrates achieving complete conversion albeit moderate yields (Scheme 11). A catalytic cycle was proposed that suggests the addition of the catalyst $KP(O)Mes_2$ across C≡C bond acquiring an active five-membered intermediate. The addition of dimesitylphosphine oxide affords the hydrophosphorylated product. An additional degradation reaction is observed in the final product when the trimethylsilyl substituted alkyne is used. This degradation reaction is prevented by altering the alkyne substrate with sterically hindered groups, to oppose the proximity of the phosphine oxide moiety and silicon atom.





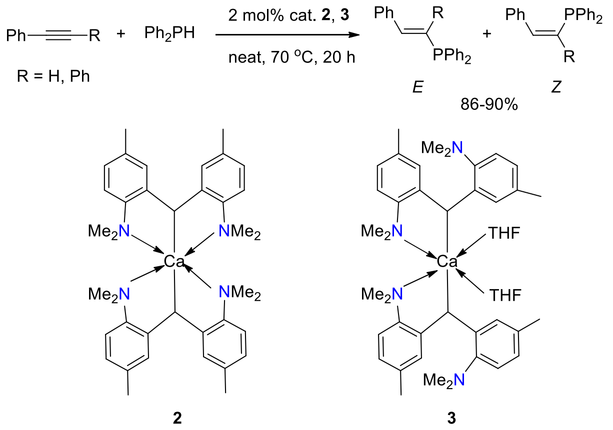
Scheme 11. $KP(O)Mes_2$–catalyzed hydrophosphorylation reaction on alkynes. The degradation reaction is shown for the trimethylsilyl-substituted alkyne substrate (R_2 = $SiMe_3$).

Very recently, Webster and co-workers demonstrated a facile route to obtain double hydrophosphorylated products. 10 mol% potassium hexamethyldisilazide (KHMDS) catalyzed the hydrophosphination of functionalized terminal alkynes with $HPPh_2$ under mild reaction condition and readily generated a series of 1,1-diphosphines with moderate to good yields (Scheme 12).[57] Altering the phosphine reagent to phenylphosphine provided quantitative yields of *P,P*-divinylphosphines, displaying a change in reactivity. A previous discussion demonstrated by Panda research group, Scheme 4 also describes the facile process of P–H bond addition to alkynes by diphenylphosphine oxide catalyzed by alkali metal hexamethyldisilazide, leading to excellent yields of the corresponding double-hydrophosphorylated product (Scheme 4-5).[48]



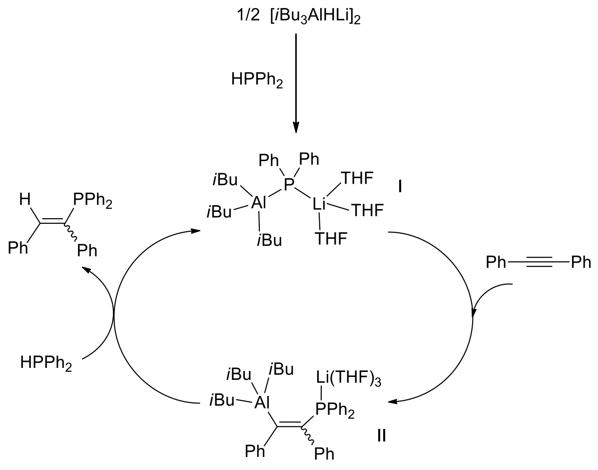
Scheme 12. KHMDS mediated double hydrophosphination of terminal alkynes.

Quite recently, the Trifonov research group focused on developing tridentate Ca(II) and Ln(II)–based pincer-type complexes. They documented the first examples of diphenylmethanido based Yb(II), Sm(II), and Ca(II) metal complexes and studied their catalytic efficiency toward hydrobenzylation, hydrosilylation, hydrophosphination, hydroamination, and hydrothiolation of C–C unsaturated bonds.[58] All the complexes exhibited 100% regioselective anti-Markovnikov addition products for the intermolecular hydrophosphination of phenylacetylene with diphenylphosphine, although utilizing Ca(II) complexes achieved 86–90% yield (Scheme 13).



Scheme 13. Ca(II)-pincer complexes for intermolecular hydrophosphination of alkynes.

The Westerhausen research group in a recent study demonstrates the efficacy of heavier alkali and alkaline earth metal bis(hexamethylsilyl)amides toward the Pudovik reaction, leading to the generation of mono- and bis-phosphorylated products.[59] The reaction of dimesitylphosphine oxide with phenylacetylene in presence of Li(HMDS) along with $Mg(HMDS)_2$, $Ca(HMDS)_2$, and $Sr(HMDS)_2$ did not prove to be efficient for the reaction. However, the reactivity was slightly lower with K(HMDS) and $Ba(HMDS)_2$, and highly reactive in presence of Rb(HMDS) and Cs(HMDS). The research group also documented the progress of P–H bond addition to alkynes and heterocumulenes in a recent book chapter.[60]

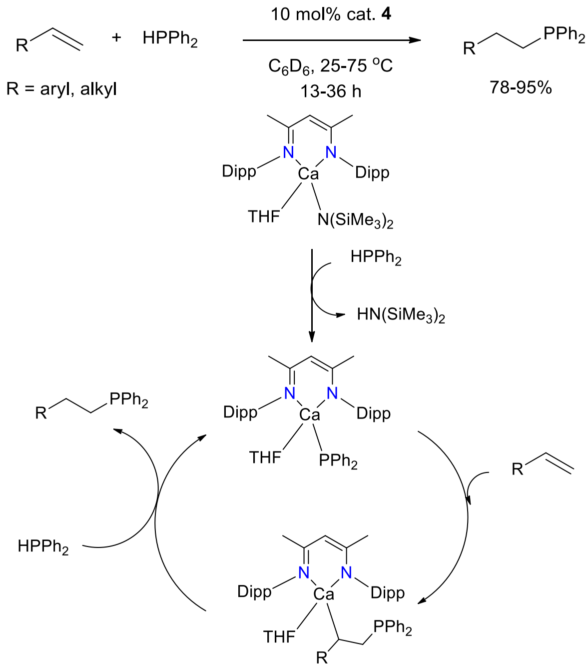


Scheme 14. The proposed mechanism for hydrophosphination of diphenylacetylene catalyzed by lithium phosphido-aluminate.

The development of *p*-block metal catalysts for the addition of P–H bonds to alkyne substrates has been limited. Nonetheless, Mulvey and his team successfully synthesized and isolated the first bimetallic main group metal catalyst, lithium phosphidoaluminate as a highly effective catalyst for use in the hydrophosphination of alkynes, alkenes, and carbodiimides.[61] 72-99% yield of hydrophosphinated products were achieved from terminal and internal alkynes. Scheme 14 displays the proposed mechanism in which active catalyst I was generated by deprotonation of diphenylphosphine by $(iBu_3AlHLi)_2$. The insertion of diphenylacetylene takes place into the Al-P bond of I. Protonolysis follows by the subsequent addition of $HPPh_2$ affording the hydrophosphinated product.

2.3. P–H bond addition to alkene substrates.

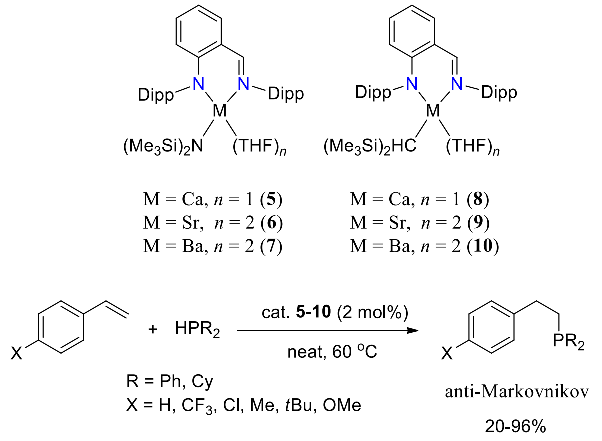
Over the years, several alkali and alkaline earth metal catalysts have gained recognition in a range of processes for the addition of P–H bonds to alkenes, when the landmark contribution was received from Hill, Trifonov, and Carpentier research groups. Hill and his coworkers initiated the breakthrough in the synthesis of C–P bonds when they developed the β-diketiminato calcium complex **4** as a competent catalyst for the addition of diphenylphosphine across a vinyl bond in styrene under ambient reaction conditions to yield anti-Markovnikov derivatives with high yields upto 95%.[62] The limitation in substrate scope encouraged the growth of novel catalysts. The calcium complex was effective although required a prolonged reaction time of 36 hours and a temperature of 75 °C to provide the hydrophosphorylated product.



Scheme 15. The reaction scheme and the proposed mechanism for hydrophosphination of styrene promoted by Ca(II) catalyst **4**.

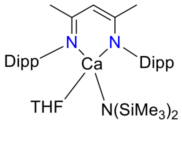
The postulated mechanism in scheme 15 suggested the formation of active Ca(II)-phosphinite pre-catalyst via σ–bond metathesis by the reaction of **4** and $HPPh_2$. The intermolecular insertion of the alkene follows into Ca-P bond. The final hydrophosphinated product is achieved by the reaction of another molecule of phosphine oxide as shown in scheme 15. As previously discussed, Cui research group has documented that calcium metal complex **1** with a tridentate ligand, was found to be an effective catalyst for the intermolecular hydrophosphination of alkenes and terminal alkynes.[52] 2 mol% of catalyst 1 provided carried out hydrophosphination of styrene, as well as bulky substrates such as *cis*-stilbene and α-methylstyrene. 1,4-addition products were achieved as the major regioselective products from isoprene and 1,3-dienes with 72-100% conversion.

In the year 2013, Carpentier and Sarazin developed a series of alkaline earth metal complexes supported by β-diketiminato and imino-anilido ligands **5**-**10**, which are highly efficient in the hydrophosphination of styrene, with diphenylphosphine and dicyclohexylphosphine as reagents, and obtained products with anti-Markovnikov regioselectivity with substrate conversion in the range of 20-96% (Scheme 16).[63] The reaction was carried out using 2 mol% catalyst loading under mild conditions. The efficacy of the imino-anilido-derived complexes was higher than that of β-diketiminato complexes. Ae-alkyl complexes were more beneficial than Ae-amide complexes in the reaction strategy.

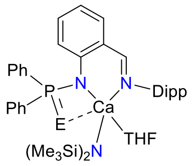


Scheme 16. β-diketiminato and imino-anilido precatalysts for hydrophosphination of styrenes.

Further improvement to precatalysts **4** and **5**–**10** was carried out by making an alteration to the protocol and using the chalcogen-derived PN-ligand, developed by the research team of Panda and Carpentier.[64] The heteroleptic calcium complexes [{$Ph_2P(E)$-N-C_6H_4-CH=N(2,6-*i*Pr_2-C_6H_3)}$CaN(SiMe_3)_2$·(THF)] (E = O, S, Se) **11** as displayed in figure 3 was proficient at P–H bond addition to styrene substrates. The molecular structure of complex **11** has been displayed in figure 4. Low to high conversion (16-94%) of the anti-Markovnikov addition products were observed under solvent-free conditions at a temperature of 60 °C analogous to scheme 16.

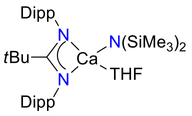


Hill *et al.*[62] (**4**)

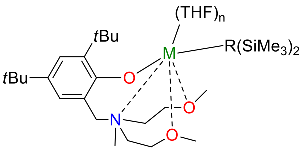


E = O, S, Se

Panda & Carpentier *et al.*[64] (**11**)

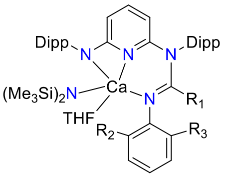


Trifonov *et al.*[65] (**12**)



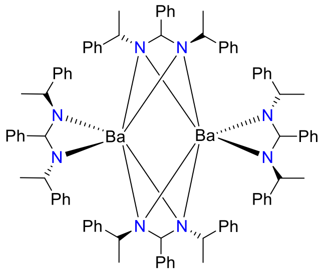
M = Ca, R = N, n = 0 (**13**)
M = Ca, R = CH, n = 1 (**14**)
M = Sr, R = CH, n = 0 (**15**)

Trifonov & Carpentier *et al.*[66]



R_1 = Me, R_2, R_3 = *i*Pr (**16**)
R_1 = CF_3, R_2 = OMe, R_3 = H (**17**)
R_1 = CF_3, R_2 = F, R_3 = H (**18**)
R_1 = CF_3, R_2 = H, R_3 = H (**19**)

Trifonov *et al.*[69]



Roesky *et al.*[67] (**20**)

Figure 3. Various efficient group 1 and 2 metal catalysts for P–H bond addition to alkene substrates.

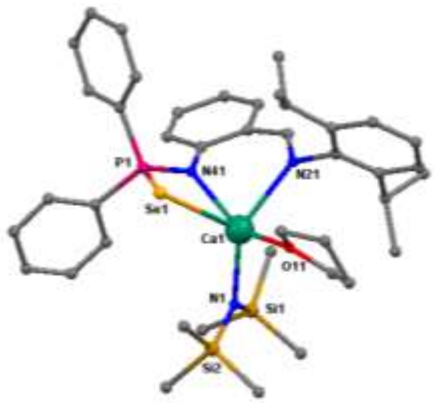
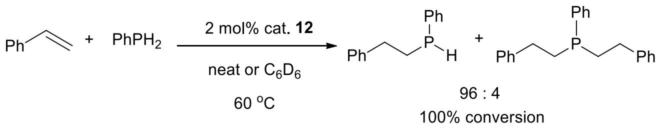


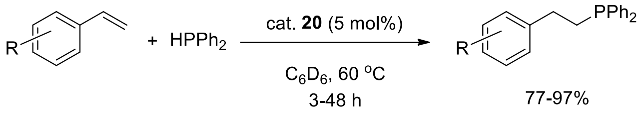
Figure 4. Efficient heteroleptic Ca(II) complex **11** for hydrophosphination of styrene derivatives. CCDC No. 1479904. See Ref. 64.

On a different note, Trifonov *et al.* isolated heteroleptic Ca(II) and Ln(II) complexes derived from amidinate ligands.[65] 2 mol% catalyst loading of the Ca(II) complex **12** enhanced the catalytic activity for the addition of $HPPh_2$ to the styrene. The reactivity of the complexes was observed to be Ca > Sm > Yb. A mixture of secondary and tertiary phosphine products was afforded from the hydrophosphination of styrene with phenylphosphine. Nonetheless, catalyst **12** provided a secondary phosphine product with high chemoselectivity with complete conversion as shown in scheme 17. Similar reaction protocol carried out with diphenylphosphine as the reagent, solely afforded regiospecific secondary phosphine product. Additionally, Trifonov, Basalov, and Carpentier research team provided a reaction protocol for the intermolecular hydrophosphination of styrene derivatives with high TON mediated by Ca(II) and Sr(II) amino-ether phenolato amido complexes **13**–**15** (Figure 3).[66] Alike scheme 17, the catalyst **15** was recognized to be highly competent toward achieving the anti-Markovnikov regiospecific, secondary phosphine product with 100% conversion. However, the reaction strategy provided the best results using crown ether–derived Yb(II) metal catalyst and thus the proposed mechanism was provided with the latter.



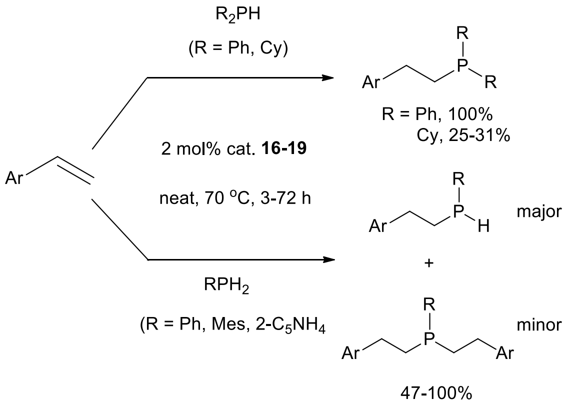
Scheme 17. Hydrophosphination of styrene by heteroleptic Ca(II) catalyst **12**.

On a parallel note, Roesky and coworkers derived homoleptic chiral benzamidinato alkaline-earth metal complexes for the promotion of hydrophosphination on vinylarenes as shown in scheme 18.[67] The requirement of prolonged reaction times were attributed to the absence of leaving group and thus moderate to good yields of the products were achieved. The Ba pre-catalyst **20** acquiring the uncommon "side-on" bridging mode was observed to display the highest efficiency than the other Ca(II) and Sr(II) congeners. The increase in the ionic radius of the central metal atom in Ba(II) metal complex explains the highest catalytic activity. Over the same period, Ward and Hunt published the first elaborate computational studies of the mechanistic details for hydrophosphination reactions on styrene and 2-vinylpyridine catalyzed by the β-diketiminato Ca(II) complex **4**.[68] The ancillary ligand was modified and simplified in the computational model. The results revealed an outer sphere conjugative addition mechanism occurs when alkene insertion takes place. The styrene moiety coordination entails Ca and π interaction from the aryl group.



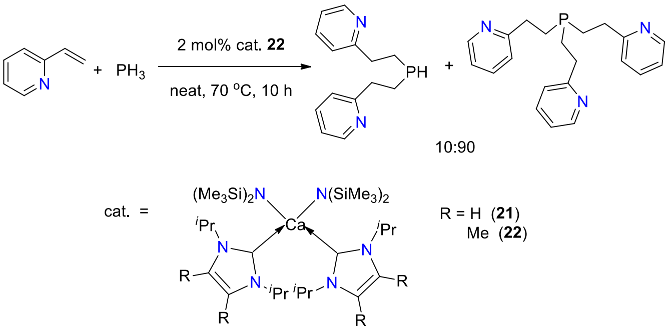
Scheme 18. Homoleptic Ba(II) catalyst **20** mediated C-P bond formation from styrene substrates.

The marvelous achievement by the Trifonov and coworkers toward the hydrophosphination reaction of alkenes mediated by alkali-earth metal and Ln(II) catalysts motivated them to continue their similar research work. Hence, later in 2018, a series of tridentate amidine-amidopyridinato supported Ca(II) complexes **16**-**19** for hydrophosphination of olefins with various primary and secondary phosphines.[69] Scheme 19 sets out the series of Ca(II) catalysts that displayed high catalytic activity affording regioselective anti-Markovnikov products with the variety of phosphines for the hydrophosphination of styrene. The hydrophosphination of inert 1-nonene with diphenylphosphine became the most valuable finding, achieving 40% conversion.



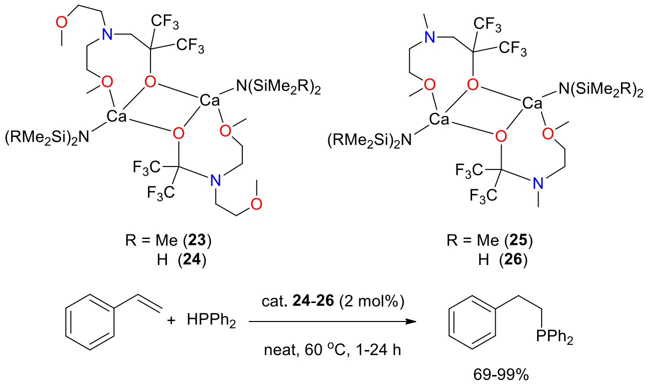
Scheme 19. Hydrophosphination of olefins by Ca(II) catalysts **16**-**19**.

Quite recently, the group established the first example of proficient intermolecular hydrophosphination of alkenes and alkynes promoted by Ca(II) bis(amido)-NHC complexes **21**-**22** and Ln(II) catalysts in the presence of PH_3 under ambient conditions.[70] Catalytic efficiencies of free NHCs was also observed for the hydrophosphination reaction, although with slower reaction rate. Regioselective anti-Markovnikov products were obtained. The detailed mechanism and kinetic studies are yet to be explored. The reaction of PH_3 with excess 2-vinylpyridine although being complicated, afforded a high yield of tris(2-(pyridin-2-yl)ethyl)phosphine using catalyst 21 (Scheme 20). Ln(II) and Ca(II) complexes were also developed from bulky benzhydryl ligands that displayed high catalytic activity and acquired outstanding regioselectivities and chemoselectivities for hydrophosphination of C–C multiple bonds in the presence of primary and secondary phosphines.[71] 4 mol% of the Ca(II) catalyst was subjected to the hydrophosphination of styrene derivatives, *Z*(*E*)-stilbene alike scheme 19 and showed high catalytic activity to afford corresponding C-P bonds.



Scheme 20. Hydrophosphination of 2-vinylpyridine by Ca(II)-NHC catalysts **21**-**22**.

The reports of P–H bond addition to alkene derivatives with pre-catalysts supported by oxygen-based ligands are scarce. Nonetheless, initial attempts by Sarazin and Carpentier were successful in the isolation of calcium-amido metal complexes **23**-**26** supported by fluorinated amino ether alcohols, that facilitated the regioselective formation of $PhCH_2CH_2PPh_2$ from styrene.[72] Intramolecular Ca···H-Si agostic interactions were exhibited in the bimetallic calcium complexes. 2 mol% of the catalysts **24**-**26** under neat and 60 °C promised to afford high TOF values with conversion in the range 69-99% from the reaction protocol (Scheme 21). However, complex **23** was not used as the suitable pre-catalyst as it was found unstable under the catalytic conditions. Later in 2018, Harder research group developed Sr(II) and Ba(II) metal complexes derived from tetranuclear siloxide/amide clusters for a broad range of hydrofunctionalization reactions, involving alkene hydrophosphination.[73] The coordination of the siloxide/amide and THF ligands to the Sr_4O_4 cube of the metal complexes **27**-**28** are shown in figure 5. The tetranuclear cluster of Ba_4O_4 **29** albeit was achieved with lower yields, displayed better catalytic activity than Sr-clusters for hydrophosphination of styrene and disubstituted alkene with complete substrate conversion.



Scheme 21. Modified calcium amide complexes **23**-**26** promoted P-H bond addition.

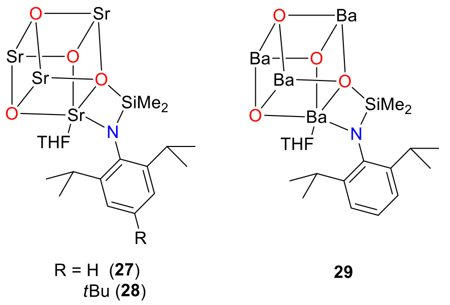
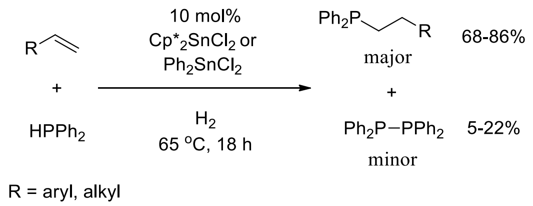


Figure 5. Alkaline-earth metal tetranuclear clusters for P–H bond addition to the alkenes. (Only one $(Dipp)NSiMe_2O^{2-}$ anion is displayed for clarity)

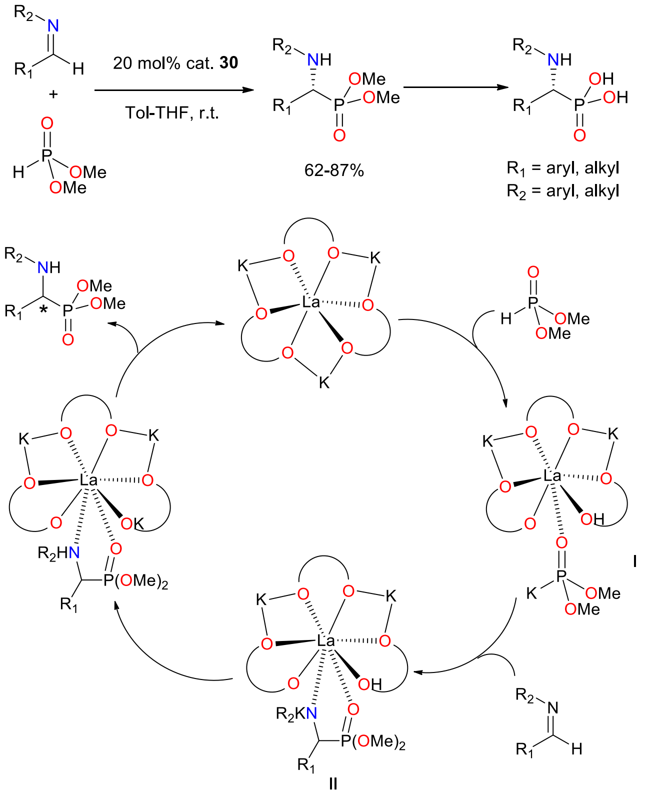
The scarcity of efficient *p*-block metal catalysts for the synthesis of C–P bonded product derivatives encouraged the proper designing and development of several p-block metal catalysts. Waterman *et al*. documented that simple $Cp^*{}_2SnCl_2$ and Ph_2SnCl_2 catalysts displayed effective reactivity for hydrophosphination of alkenes under the H_2 atmosphere and afforded major monophosphinated product with good yields up to 86% (Scheme 22).[74] Nonetheless, $(PPh_2)_2$ was also obtained as a minor competitive dehydrocoupling product up to 15% yield when the reaction protocol was carried out under H_2 atmosphere. The stoichiometric reaction to isolate $Cp^*{}_2Sn(PPh_2)_2$ resulted in the decomposition to $(PPh_2)_2$. As previously discussed, lithium phosphidoaluminate proved as a proficient catalyst for the hydrophosphination of alkynes, alkenes, and carbodiimides.[61] Anti-Markovnikov products were achieved in presence of a 10 mol% catalyst and required an elevated temperature of 110 °C. Interestingly, vinyl Bpin underwent P-H addition effectively to afford 93% of linear phosphine boronic ester.



Scheme 22. Sn(IV)-catalyzed hydrophosphination of alkenes.

2.4. P–H bond addition to compounds with C=O and C=N functional groups.

For many years, considerable growth in C–P bond formation from various unsaturated C=O and C=N groups of aldehydes, ketones, aldimines, and enones mediated by *s*- and *p*-block metal catalysts have been noted. The Shibasaki group first introduced the synthesis of optically active *α*-amino phosphonic acids promoted by versatile heterobimetallic lanthanum-potassium-BINOL complex **30** (figure 6) via hydrophosphonylation of imines. Scheme 23 shows the asymmetric catalyst induced the P–H bond addition and moderate to high enantiomeric excess of *α*-amino phosphonic acids were achieved.[75]



Scheme 23. Heterobimetallic catalyst **30** promoted asymmetric hydrophosphonylation of imines and the proposed catalytic cycle.

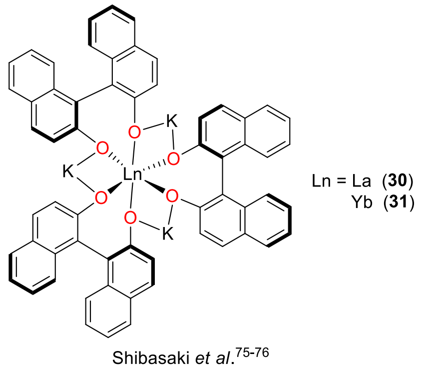
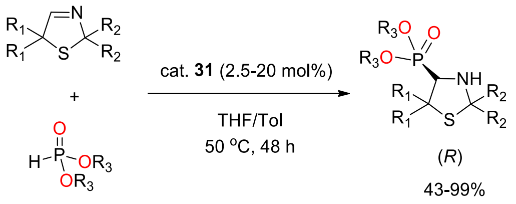


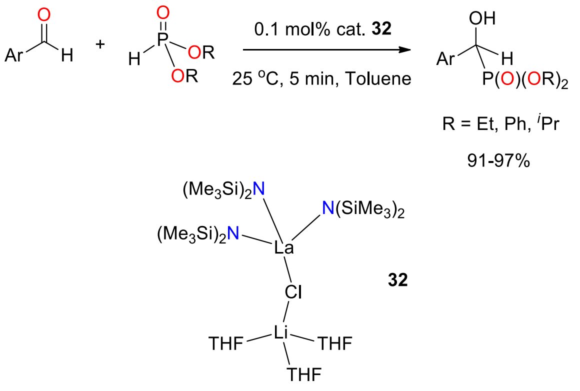
Figure 6. Heterobimetallic Ln-K catalysts developed by Shibasaki research group.

A catalytic cycle was proposed in which the deprotonation of $HP(O)(OMe)_2$ generates an active $KP(O)(OMe)_2$ intermediate (I). The imine substrates add to (I) producing an optically active potassium salt of α-amino phosphonates. Furthermore, the group ascertained the first report of enantioselective catalytic hydrophosphonylation of cyclic imines in presence of a similar heterobimetallic complex **31** (figure 6) as displayed in scheme 24. The catalyst efficacy was improved by involving a series of linear as well as cyclic phosphonates with cyclic imines. A library of thiazolidinyl phosphonates was obtained with excellent optical purity and chemical yields up to 99%.[76]

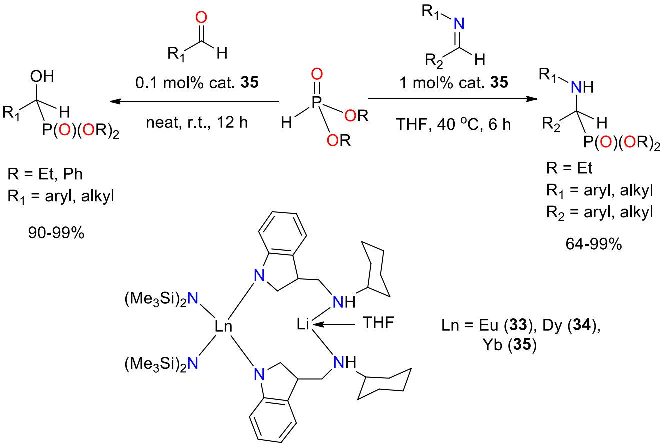


Scheme 24. Yb-K-mediated enantioselective hydrophosphonylation of cyclic imines.

Shen working group reported a highly potential tetracoordinate lanthanum amide complexes $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ to achieve α-hydroxyphosphonates via Pudovik reaction (Scheme 25).[77] The addition of diethylphosphite to aryl aldehydes was carried out in toluene and 0.1 mol% of $[(Me_3Si)_2N]_3La(\mu\text{-}Cl)Li(THF)_3$ **32**. Excellent yields of the products (> 90%) were afforded within five minutes of reaction time at room temperature. The improved efficiency of $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ as compared to $Ln[N(Me_3Si)_2]_3$ was attributed due to the presence of LiCl that behaves as Lewis acid. Carpentier and Sarazin mentioned the first report on the proficiency of $[Ae\{N(SiMe_3)_2\}_2(THF)_2]$ (Ae = Ca, Sr, Ba) and other well-defined catalysts **4**, **5**–**7**, and **14** toward C–P bond formation from aldehydes and nonactivated ketones alike scheme 25 with substrate conversion in the range 55-96%.[78] 0.05–0.1 mol% of the catalysts proved to be highly effective for hydrophosphonylation to obtain the desired products by the addition of diethylphosphite.



Scheme 25. Hydrophosphonylation of aldehydes promoted by catalyst **32**.

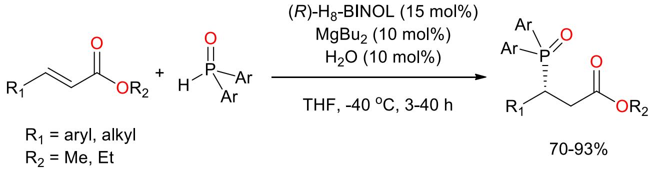


Scheme 26. Bimetallic Ln–Li complexes mediated hydrophosphonylation of aldehydes and imines.

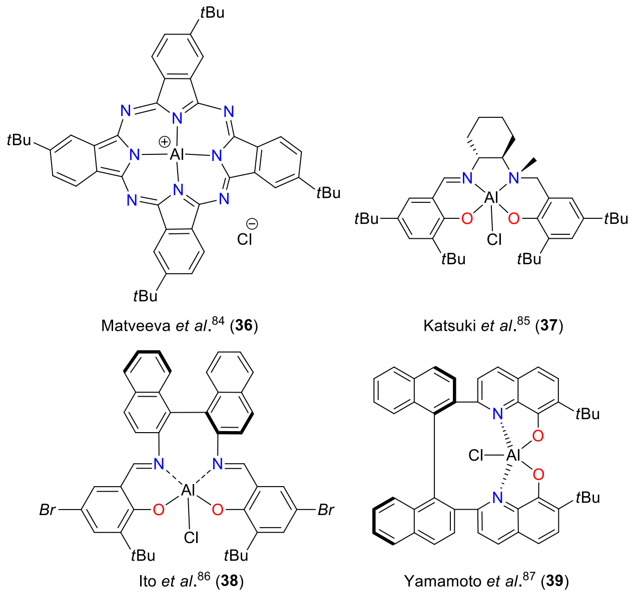
Alongside, Wang *et al*. isolated lanthanide amido complexes **33**–**35** from bis(indolyl) ligands having an amino-coordinate-lithium bridge.[79] The complexes exhibited high catalytic activity during the hydrophosphonylation of aliphatic and aromatic aldehydes and aldimines under solvent-free and THF conditions respectively (Scheme 26). Complex **35** was chosen as the favorable catalyst and 0.1 mol% could undergo the C-P bond formation from aliphatic and aromatic aldehydes at room temperature providing excellent yields. However, aldimines were reduced in presence of 1 mol% of **35** at 40 °C for 6 hours and moderate to high yields were obtained.

Chiral Mg(II) binaphtholate aqua complexes were envisioned by the Ishihara research group as effective catalysts for the enantioselective 1,4-hydrophosphorylation and 1,2-hydrophosphonylation of α,β-unsaturated esters, and ketones respectively.[80] (R)-H_8-BINOL/Mg(II) aqua complex could be obtained *in situ* and functioned as cooperative Brønsted/Lewis acid-base catalyst. Scheme 27 demonstrates the 1,4-hydrophosphorylation on a series of alkyl cinnamates with diaryl phosphine oxides proceeded smoothly from which high enantioselective products up to 96% and quantitative chemical yields up to 93% were achieved. Additionally, 1,2-hydrophosphonylation of unactivated α,β-unsaturated ketones with dialkyl phosphites were successfully carried out in presence of the catalyst. A reaction methodology with commercially available *n*-

butyllithium was reported which facilitated hydrophosphonylation of aldehydes and unactivated ketones with low catalyst loading (0.1–0.5 mol%) under solvent-free conditions and shorter reaction time.[81] A wide variety of substrate scope afforded α-hydroxyphosphonates with yield up to 99% and high TOF. Meanwhile, a base-catalyzed hydrophosphinylation was executed by Zhao and coworkers. K_2CO_3 was recognized as a precatalyst for the addition of optically pure *H*-phosphinates to ketones to afford stereogenic tertiary α-hydroxyphosphinates, although this reaction procedure required higher catalyst loading of 25 mol% and extended reaction time providing moderate to high yields upto 98%.[82] Acyclic aliphatic ketones however displayed sluggish selectivities.



Scheme 27. Chiral Mg(II) binaphtholate aqua complex promoted 1,4-hydrophosphorylation of α,β-unsaturated esters.

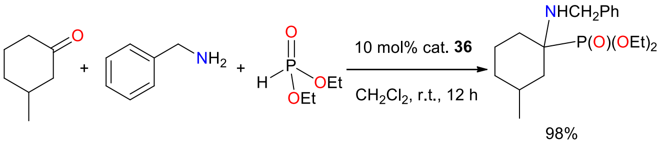


Matveeva *et al.*[84] (**36**) Katsuki *et al.*[85] (**37**)

Ito *et al.*[86] (**38**) Yamamoto *et al.*[87] (**39**)

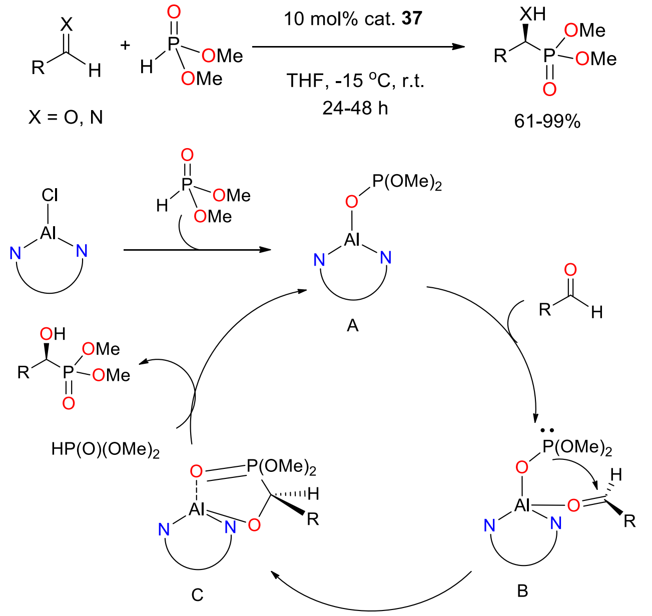
Figure 7. Versatile Al(III) catalysts for C-P bond formation.

A breakthrough of the P-H bond addition to unsaturated substrates was investigated with *p*-block metal precursors on a parallel note, and a series of Al(III) catalysts have gained the recognition to furnish corresponding organophosphorus compounds. A versatile tetra[*tert*-butyl)pthalocyanine] aluminum chloride (*t*PcAlCl) **36** (figure 7) was developed by Matveeva *et al.* to conduct a three-component one-pot synthesis (Kabachnick-Fields reaction). Moderate to good yields of α-aminophosphonates were offered by the Al(III) catalyzed one-pot reactions of cyclic ketones, benzylamine, and diethyl phosphite.[83-84] An example of the reaction protocol providing 98% yield of the product has been shown in scheme 28.



Scheme 28. (*t*PcAlCl)-mediated Kabachnick-Fields reaction.

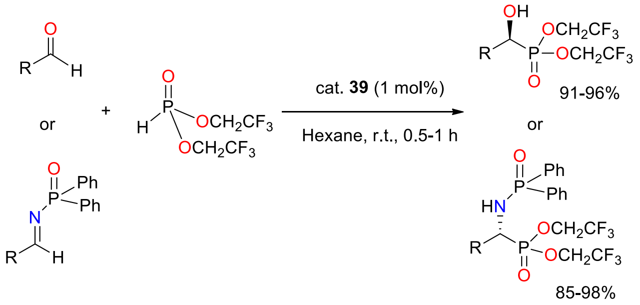
Katsuki and co-workers reported excellent yields of enantiomeric (*S*)-α-hydroxy and α-amino phosphonates by utilizing aluminum (salalen) complex **37** (figure 7) through asymmetric hydrophosphonylation of aliphatic and aromatic aldehydes and aldimines. 10 mol% of **37** at -15 °C or room temperature afforded the corresponding high enantioselective hydrophoshonylated products from a series of aldehydes and aldimines in presence of dimethyl phosphite.[85] The proposed mechanistic cycle is demonstrated in scheme 29 that reveals the reaction of dimethyl phosphite to **37** undergoes chloride exchange, producing an active Al-phosphite species A. The addition of aldehyde takes place coordinating via carbonyl substituent. Intermolecular addition followed by the addition of $HP(O)(OMe)_2$ affords (*S*)-α-hydroxy-phosphonates species.



Scheme 29. Al(III)-catalyzed enantioselective hydrophosphonylation of aldehydes and aldimines.

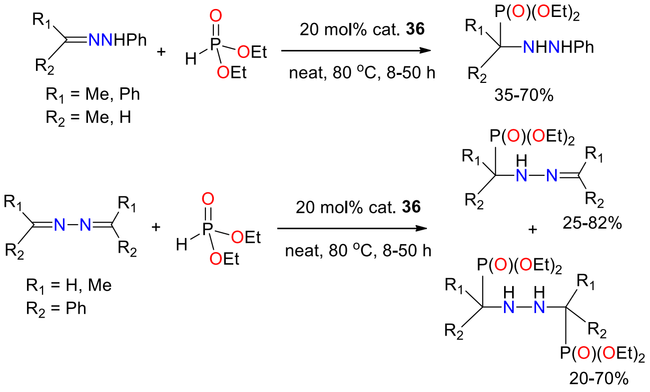
Alongside, similar hydrophosphonylation of aromatic and aliphatic aldehydes was also demonstrated by an aluminum binaphthyl complex **38** (figure 7) analogous to **37**. Moderate to good enantioselective products and yields in the range 55-100% were achieved in presence of 10 mol% of **38** in THF at room temperature.[86] The presence of binaphthyl group induces strong chiral auxiliary and thus the Al(III) complex displays asymmetric catalysis effectively. Yamamoto research group published a tethered bis(8-quinolato)(TBOx) Al(III) complex **39** proficient toward the catalytic Pudovik reaction of aldehydes and imines (Scheme 30).[87] High yields and high enantioselective α-hydroxy and α-aminophosphonates were obtained using low catalyst loading (0.5-1 mol%) under ambient conditions. The reaction protocol optimized with bis(2,2,2-

trifluoroethyl) phosphite with benzaldehyde provided the best result in presence of **39**, and thereby a variety of aldehydes and *N*-Diphenylphosphinoyl substituted aldimines were subjected for the hydrophosphonylation reaction that afforded excellent yields of the respective products.



Scheme 30. Effective TBOx-Al(III) complex **39** for enantioselective hydrophosphonylation of aldehydes and aldimines.

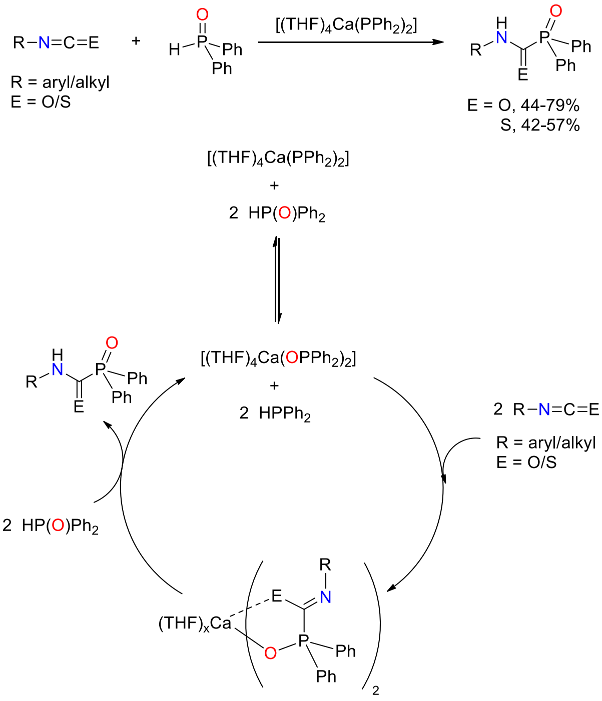
Constructive asymmetric hydrophosphonylation of carbonyl compounds was also executed by readily available Et_2AlCl, supported by bifunctional chiral ligands. The broad substrate scope of aldehydes and first report with trifluoromethylketones with dialkyl phosphite proceeded smoothly providing excellent yields of α-hydroxy phosphonates and quarternary α-hydroxy trfluoromethyl phosphonates respectively with good enantioselectivities.[88-89] Matveeva research group has developed catalyst **36** as an effective catalyst for P-H bond addition to carbonyl compounds. The catalyst was furthermore used for hydrophosphonylation of hydrazones and azines (Scheme 31).[90] The variation of aliphatic, aromatic, and cyclic azine substrates with diethyl phosphite in presence of 20 mol% **36** at higher temperature and prolonged reaction time provided corresponding mono- and bis-hydrophosphonylated products with low to moderate yields, confirmed from ^{31}P NMR spectra. The published research work motivated the scientists to accumulate and thus elaborate review articles providing a range of metal-mediated asymmetric C–P bond formations from unsaturated compounds were presented by Herrera and coworkers in 2008 and Zhao and Wang in 2012.[91-92]



Scheme 31. Hydrophosphonylation of hydrazones and azines promoted by Al(III) catalyst **36**.

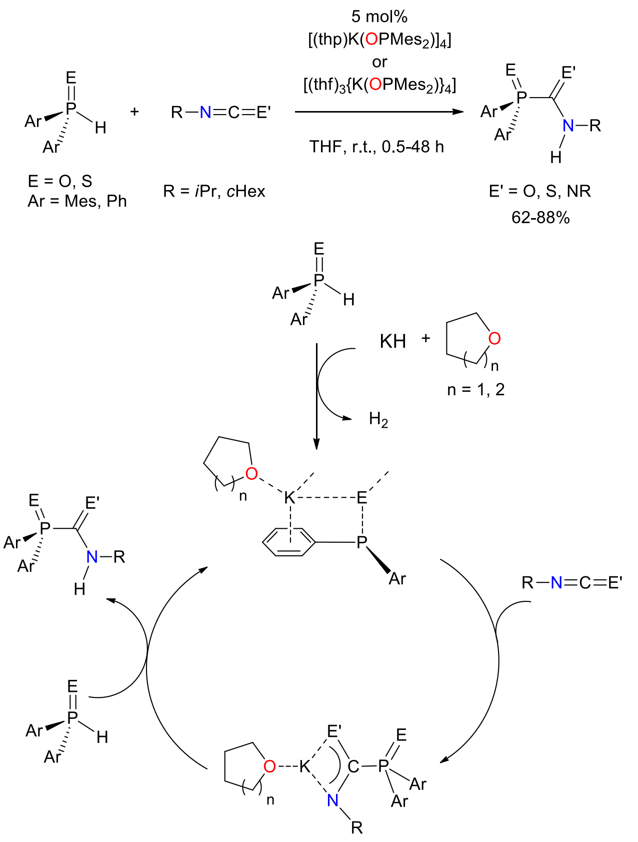
2.5. P–H bond addition to heterocumulenes.

The catalytic hydroelementation of heterocumulenes is many challenging and hence scarce reports are available to date. The versatile catalysts recognized by various research groups have been discussed. Hill research group previously published the effective homoleptic complexes $[Ae\{N(SiMe_3)_2\}_2(THF)_2]$ (Ae=Ca, Sr, Ba) and heteroleptic complex **4** for hydrophosphination of alkene derivatives. The complexes were further exploited for hydrophosphination of carbodiimides with diphenylphosphine, di-*p*-tolylphosphine and dicyclohexylphosphine.[93] A range of symmetric and unsymmetric carbodiimides were subjected to C–P bond synthesis with excellent yield up to 99% at room temperature in the presence of 1.5 mol% of **4**, the simpler $[Ae\{N(SiMe_3)_2\}_2(THF)_2]$ catalysts were more reactive to afford the phosphaguanidines. Motivated from the result, Westerhausen research group followed the landmark contribution toward P–H bond addition and examined the role of $[(THF)_4Ca(PPh_2)_2]$ as a powerful catalyst for hydrophosphorylation of organic isocyanates and isothiocyanates. The reaction of diphenylphosphine oxide and a slight excess of isocyanates and isothiocyanates in presence of 5 mol% of the catalyst in THF at room temperature afforded *N*-organyldiphenylphosphorylformamides and thioformamides in moderate yields.[94] Scheme 32 demonstrates the catalytic cycle suggests that the formation of calcium bis(diphenylphosphinite) is the active pre-catalyst on which the addition of R-N=C=E (E = O/S) takes place. Further addition of diphenylphosphine affords the product.



Scheme 32. The proposed mechanism for Ca(II)-mediated hydrophosphorylation of isocyanates and isothiocyanates.

Albeit not a catalytic methodology, yet a base mediated direct synthesis of chiral and achiral phosphaguanidine boranes gained recognition from Busacca and Wipf research group.[95] The reaction of secondary phosphine-boranes with carbodiimides afforded phosphaguanidine boranes in presence of NaH under ambient condition. *n*-BuLi as the base for the reaction provided low to moderate yields. In addition, reactivity corresponding phosphines were also achieved from deborination of phosphaguanidines.



Scheme 33. Potassium-catalyzed hydrophosphorylation of heterocumulenes and the proposed catalytic cycle.

Most recently, Westerhausen and coworkers demonstrated versatile alkaline-earth metal complexes Ar_2POK – $[(thp)K(OPMes_2)]_4$ and $[(thf)_3\{K(OPMes_2)\}_4]$ toward the catalytic hydrophosphorylation of heterocumulenes.[96] A detailed structural explanation of the potassium complexes has been provided. The complexes displayed complete catalytic conversion when 5 mol% was used in addition of diarylphosphine oxide and diaryphosphine sulfide to isocyanates, isothiocyanates, and carbodiimides under ambient reaction conditions affording good yields. The plausible mechanism in scheme 33 displays that the addition of heterocumulene to the active potassium catalyst and a potassium (thio)phosphinite intermediate is formed. The reaction of further Ar_2PEH (Ar = Mes, Ph; E = O, S) acquires the respective products. The studies were further extended to examine the influence of steric coordination from 18-Crown-6 ether on potassium and calcium diphenylphosphinite toward P–H bond addition on isopropyl-isocyanate with dimesitylphosphine oxide.[97] The potassium complexes displayed higher catalytic efficiency than the calcium catalysts while the coordination of the crown ether replacing the THF molecules obstructs the hydrophosphorylation reaction due to increased steric hindrance on the site of catalysis.

3. Summary

A detailed study compiling reports of a series of versatile *s*- and *p*-block especially aluminium metal catalysts utilized in several catalytic additions of P–H bonds to a wide range of unsaturated compounds, such as organic nitriles, alkynes, alkenes, aldehydes, ketones, enones, azines, and heterocumulenes, has been presented. The high abundance, economical nature, and low toxicity of these metals have paved the path for several research groups around the globe to design unique metal catalysts supported by chelating ligands and utilize them in the synthesis of C–P bonds from substrates. A variety of phosphine substrates have also been discussed, leading to variation in reaction methodologies.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes and references

Keywords: *s*- and *p*- block metal catalysts • synthesis and structure • hydroelementation reactions • unsaturated compounds • C–P bond formation

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