Hydrophosphinylation of Alkynes via Neutral Magnesium Complexes: Evidence for Ligand Dependency in Structure-Activity Relationships

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ABSTRACT:

The pursuit of practical, straightforward, and sustainable methods for forming carbon-phosphorus bonds is crucial in both academia and industry. Traditional synthetic methods often rely on hazardous, halogenated precursors through salt-metathesis routes. In this study, we have synthesized and characterized magnesium complexes [L(Mg-nBu)$_2$] (L = bis(diiminate); nBu = n-butyl) **1** and **2**. Complex **1** effectively catalyzes the hydrophosphinylation of alkynes resulting stepwise hydrophosphinylated products namely monophosphinylated vinyledene- and 1,2-diphosphinylated alkanes. While doubly addition products with the alkynes are predominant, this catalytic reaction produces anti-Markovnikov products with inactivated alkenes, whereas activated alkenes giving rise to conjugated products. This transformation showcases an excellent atom economy, broad functional group tolerance and gram scale synthesis for organophosphorus compounds. Through controlled experiments, kinetic studies, and density functional theoretical calculations, we elucidated the reaction mechanism, identifying the active catalytic species and revealing a stepwise hydrophosphinylation process of alkynes. Although complex **1** showed its potential in the hydrophosphinylation of alkynes, complexes **2** and **3** produced a lower yield of hydrophosphinylated products, indicating the role of ligand (spacer) in this catalytic transformation. This work is the first to demonstrate that a neutral magnesium complex can independently catalyse the hydrophosphinylation of alkynes

and offers opportunities for the hydrophosphinylation of other compounds catalyzed by main-group metal complexes.

Introduction

The pivotal role of transition metals in homogeneous catalysis has been well-established for years. However, their limited availability, toxicity, and high cost, have created a pressing need for alternatives. Consequently, recent years have seen a significant shift towards using cheaper and earth-abundant main group elements in catalysis as an alternative to transition metals.[1,2] In the search for non-toxic and environmentally friendly catalysts, s-block metal complexes (excluding beryllium) have gained recognition not only as effective stoichiometric reagents but also for their significant role in catalytic reactions.[3] Magnesium has attracted considerable attention due to its abundance in the Earth's crust and its varied reactivity patterns, including those associated with the intermediate oxidation state (I).[4] In catalysis, magnesium(II) complexes drive the chemical transformations through redox-invariant mechanisms such as σ-bond metathesis and the insertion of unsaturated species into the Mg−X bond (where X = reactive group).[3b-d,5] However, it is only in the past decade that magnesium-centred reactions of interest to organometallic chemists have begun to emerge. These reactions include hydroamination, hydroboration, hydrosilylation, coupling reactions, and C−H bond-activation-mediated organic transformations,[6-10] highlights the usefulness of magnesium complexes in various organic reactions.

The preparation of organophosphines and phosphine oxides, which are widely used in the pharmaceutical industry and serve as essential ligands in catalysis,[11,12] commonly follow the salt metathesis routes. This method more often requires the hazardous halogenated precursors.[13,14] Research in this field showed that the direct addition of P-H bond(s) to unsaturated substrates offers an alternative approach for the preparation of organophosphorus compounds. Although the process is more atom-economic and appealing synthetic approach,

it often requires transition-metal catalysts or radical initiators.[15] Consequently, there has been increasing interest in developing earth-abundant and sustainable catalysts for the addition of P–H bonds to unsaturated species.[16] While several transition-metal-free methods for hydrophosphination of unsaturated species exist,[17] the hydrophosphinylation reaction is a less significantly investigated topic.[18] Given the involvement of s-block metals as hydrophosphinylation catalysts, they are even rare.[19-22]

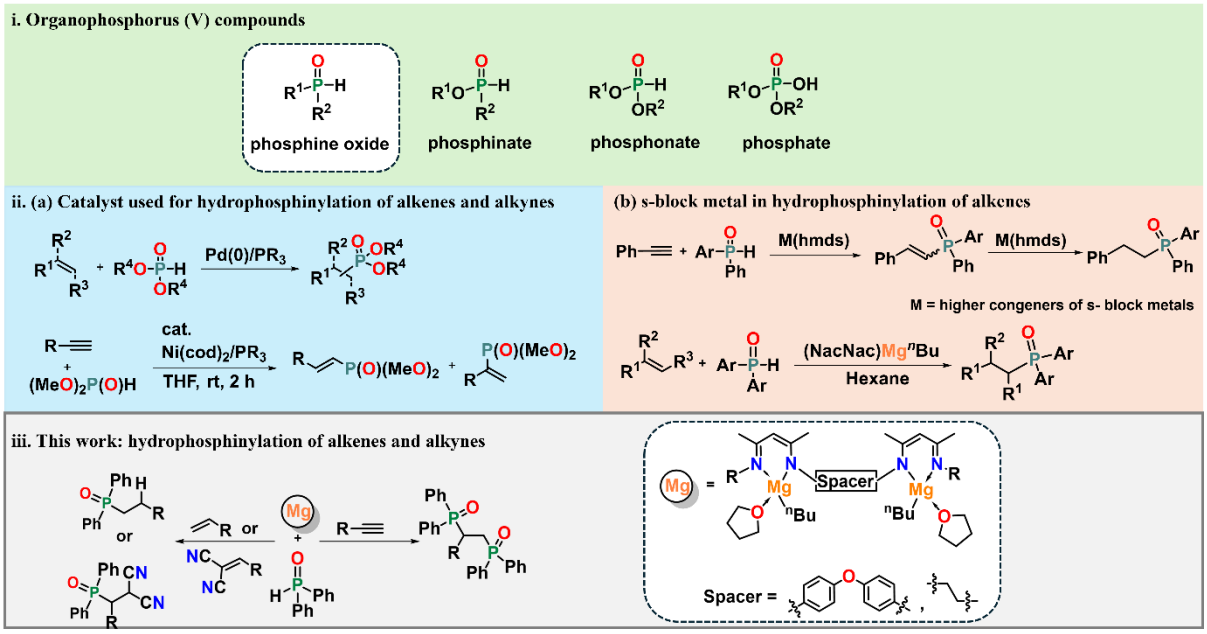


Figure 1. (i) Organophosphorus compounds used in hydrophosphinylation; (ii) hydrophosphinylation of unsaturated compounds (a) using transition metal complexes, (b) s-block metal complexes; (iii) this work.

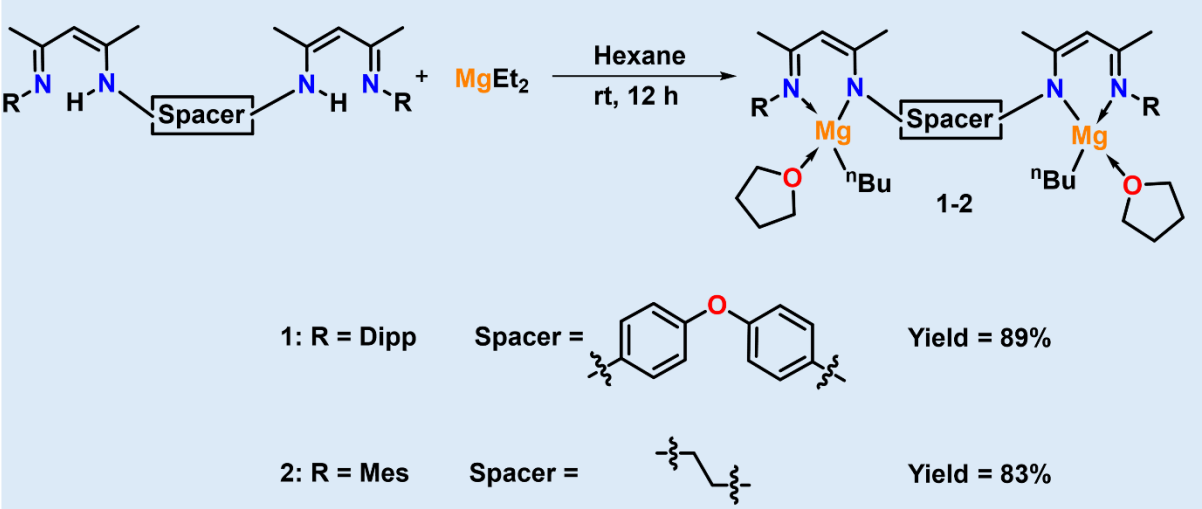
In 2020, Westerhausen demonstrated the dependency of hydrophosphinylation reaction of alkynes on the nature and size of the s-block metal complexes and they concluded that heavy alkali and alkaline earth-metal amides are acting as a better catalyst for hydrophosphinylation of alkynes whereas the Li, Mg, Ca amides did not produce any P^V-(O)-H addition product.[20] To the best of our knowledge, the hydrophosphinylation of alkynes catalysed by a neutral Mg metal complex alone has yet not been reported to date. Therefore, the imperative to develop a magnesium catalyst for the hydrophosphinylation of alkynes and alkenes, with a broad

substrate scope and accommodating a wide range of functional groups, is in the sense of exigent. In this work, we synthesized and characterized bis(diiminate)-based magnesium complexes **1** and **2** and investigated their effectiveness in the hydrophosphinylation of alkynes and alkenes with a catalyst loading of 5 mol% over a 12-hour reaction time. Controlled experiments and theoretical studies were performed to establish the reaction mechanism that showed the stepwise phosphorylated compound formation.

RESULTS AND DISCUSSION

Synthesis and characterization of magnesium complexes

Complexes **1** and **2** were synthesized by reacting corresponding bis(diiminate) ligands[23] with three equiv. of n-butyl magnesium in hexane, yielding orange solids with 89% and 83% yields, respectively (Scheme 1). Comparing the proton NMR spectra of complex **1** and **2** reveals key differences in the chemical shifts of butyl protons. The methylene (CH_2) group attached to magnesium shows a multiplet at –0.31 ppm in complex **1**, whereas in complex **2**, it is observed at 0.15 ppm. For the methyl (CH_3) protons of the butyl groups, complex **1** exhibits a triplet at 1.02 ppm, significantly upfield compared to the corresponding triplet at 2.36 ppm in complex **2**. Additionally, the remaining methylene protons of the butyl groups differ in the two complexes (see Figures S1-6). These differences in chemical shifts point out less electron density on Mg in case of complex **1** compared to complex **2** and it could be a sign of magnesium center influencing the reaction differently.



Scheme 1. Synthesis of magnesium complex **1-2**.

Hydrophosphinylation of alkynes

To optimize the reaction condition, we choose phenylacetylene and diphenylphosphine oxide as a point of reference substrate. The reaction conditions were optimized and monitored by NMR spectroscopy, and the yields were calculated based on the integration of the product and starting material in ^{1}H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard. The reaction of 2 equiv. of phenylacetylene with 4 equiv. of diphenylphosphine oxide was carried out in hexane with 3 mol% of complex **1** at rt. Until 12 hours there was not any product formation (Table 1, entries 2). When the reaction was carried out at 80 °C with the same catalyst loading (3 mol%) for 6 and 12 hours, 1,2-diphosphinylated product **4a** was obtained in 36% and 49% yields, respectively (Table 1, entries 3 and 4). In the ^{1}H NMR spectrum, three new multiplets at 2.84 ppm, 3.14 ppm and 4.27 ppm were observed, corresponding to the two methylene protons and one methine proton of the product. Further, the study showed that the increase in catalyst loading to 5 mol % and lowering the temperature to room temperature did not result in any product formation for 12 hours (Table 1, entry 5). When the reaction was performed with 5 mol % loading of **1** at 80 °C in hexane, 59% and 85% yield of **4a** were obtained after 6 hours, (Table 1, entry 6), after 12 hours (Table 1, entry 7) respectively. With

change in solvent from hexane to toluene, a 5 mol% loading of **1** at 80 °C, only 35% yield of **4a** was obtained (Table 1, entry 8) after 6 hours. When the reaction was conducted at 110 °C in toluene, the product yield decreased to 25% (Table 1, entry 9), suggesting that increasing the temperature to 110 °C adversely affects the yield of product formation. A blank experiment was conducted without **1** that showed no product formation (Table 1, entry 1), confirming the essential role of complex **1** in this hydrophosphinylation reaction.

Table 1. Optimization table for the hydrophosphinylation of alkene derivatives catalyzed by complex **1**[a].

Entry	Cat. (mol%)	Solvent	T (°C)	T (h)	NMR yield (%)
1.	-	Hexane	80	12	0
2.	3	Hexane	rt	12	0
3.	3	Hexane	80	6	36
4.	3	Hexane	80	12	49
5.	5	Hexane	rt	12	0
6.	5	Hexane	80	6	59
7.	**5**	**Hexane**	**80**	**12**	**85**
8.	5	Toluene	80	6	35
9.	5	Toluene	110	12	25
10.	5[b]	Hexane	80	12	9
11.	5[c]	Hexane	80	12	36

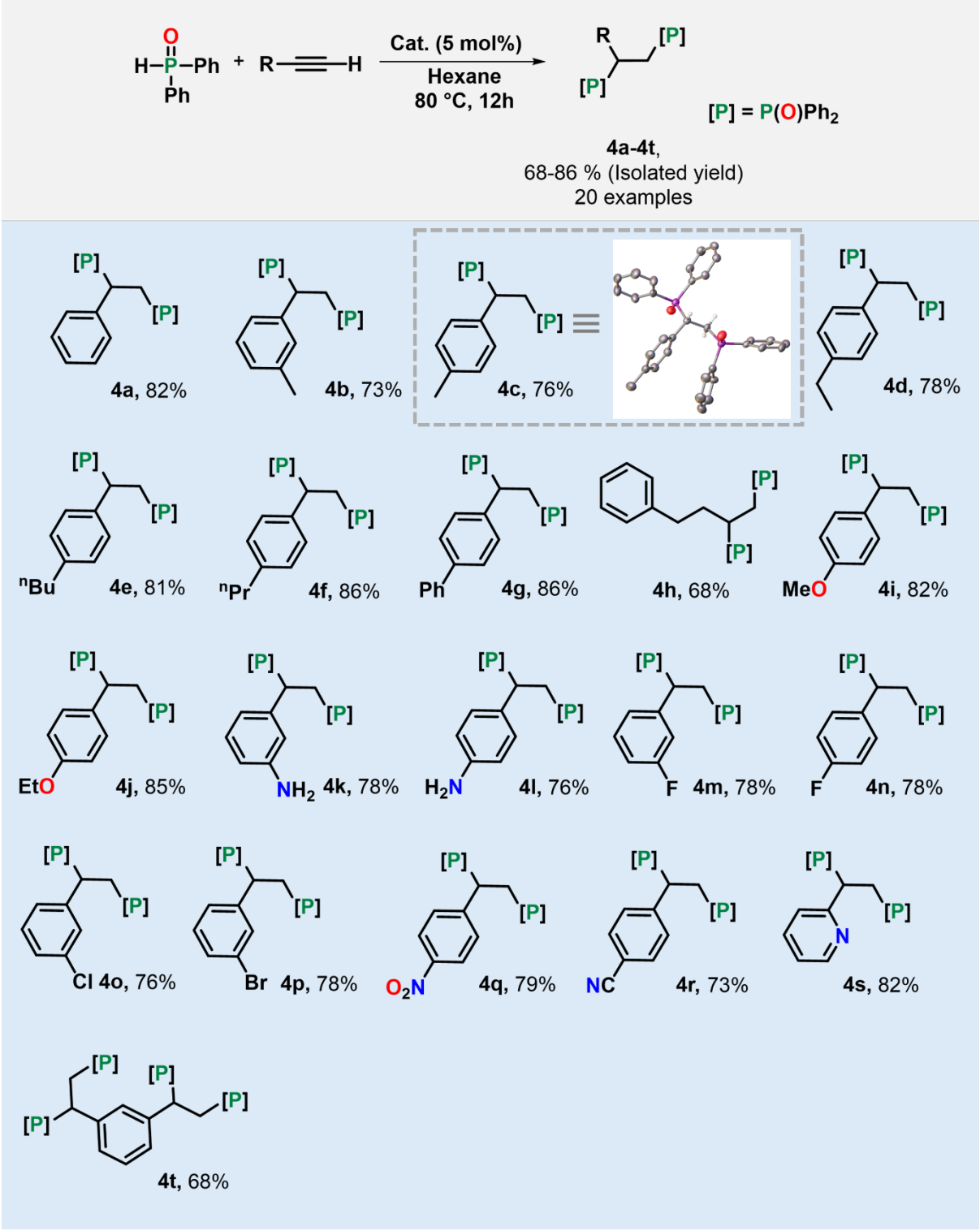
[a]Reactions were conducted with phenylacetylene (2 equiv.), diphenylphosphine oxide (4 equiv.), and complex **1** in a pressure tube. Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard; [b]With 5 mol% of Mg complex **2**; [c]With 5 mol % of Mg complex **3**.

After finding the role of magnesium complex **1** in hydrophosphinylation reaction, to establish the role of spacer, complex **2** was tested alongside complex **1** for its catalytic activity in the

hydrophosphinylation reaction. The reaction was carried out using 5 mol% of complex **2** in hexane at 80 °C for 12 hours. Surprisingly, the yield of **4a** was only 9% (Table 1, entry 10). The ^{1}H and ^{13}C NMR of complexes **1** and **2** suggest the butyl group in **1** is more electron rich compared to complex **2**. This change in electronic factor might facilitate the release of butane in the first step of the reaction. Having a similar ^{1}H NMR shift of the butyl group to that of complex **1**, and to explore the impact of a more rigid spacer, we have successfully synthesized a phenyl-bridged magnesium complex **3** with an 85% yield by following a reported procedure (see Figures S7 and S8).[25] Using standard reaction conditions, complex **3** was tested for the hydrophosphinylation reaction and interestingly, the product yield was increased to 36%. However, it is significantly lower than that of the case in complex **1.** This outcome showed that having a rigid and definite orientation of the spacer is necessary in enhancing catalytic efficiency. The oxy-bridged spacer likely provides a more optimal structural and electronic environment for catalysis, highlighting the importance of spacer design in influencing catalytic performance.

Having reached the reasoning into the requirement of complex **1**, we then went on to explore the scope of the hydrophosphinylation reaction of alkynes. Using the standard reaction conditions, we treated various alkynes which led to the formation of corresponding 1,2-bis(phosphinylated) alkane derivatives **4a-4t** in 68-86% isolated yield (Scheme 2). Phenylacetylenes containing halogen atoms at the *meta*- and *para*-position were well tolerated to give compounds **4m**–**4p** in high yields. Using the electron donating *para*-OMe, *para*-OEt, meta-NH_2, substituted phenyl acetylenes, the corresponding 1,2-diphosphinylated products **4i**–**4l** were isolated in very good yields. *Para*-NO_2, *para*-CN substituents are also well withstood to the reaction conditions, resulting in **4q** and **4r** in excellent yields. In case of 3-butynylbenzene in which the triple bond is away from the phenyl ring, a reduced yield of

diphosphinylated product **4h** was observed. We have also achieved the hydrophosphinylation of 1,3-diethynylbenzene and 3-ethynylpyridine suggesting a broad substrate scope for this



Scheme 2. Hydrophosphinylation of alkynes catalyzed by magnesium complex **1**[a].

[a]Reactions were conducted with alkyne (0.47 mmol, 2.0 equiv.), diphenylphosphine oxide ($Ph_2P(O)H$) (0.94 mmol, 4.0 equiv.), complex **1** (5 mol %) in hexane, in a pressure/sealed tube at 80 °C for 12 h.

magnesium catalyzed hydrophosphinylation reaction. Compounds **4a-4t** were well characterized with ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectroscopy and mass spectrometry. Bulk-scale synthesis is a significant challenge for industrial applications. Therefore, we conducted a gram-scale reaction to assess the feasibility of bulk-scale production. A reaction was carried out using 1.5 g of phenylacetylene in the presence of 4 equiv. of diphenylphosphine oxide (7.7 g) and 5 mol % of **1** under optimized reaction condition. This resulted in the formation of the desired product **4a** with an isolated yield of 78%. This successful scaling up reaction demonstrates the potential of **1** as a catalyst for bulk-scale synthesis (see Figure S163-165).

Kinetic Studies

To find out the rate of hydrophosphinylation reaction, the rate law for catalytic alkyne hydrophosphinylation was determined using initial rate analysis at different catalyst concentrations. We obtained the initial rate (k_{obs}) from the [product] versus time plot. Then, we plotted log(k_{obs}) against log(concentration of x) (where x represents either of **1**, $Ph_2P(O)H$, or phenylacetylene) to determine the reaction order. The initial rates (k_{obs}) were determined from the plot of [product] vs. time (see Figure S166) using various concentrations of **1** (6, 12, 18, mM) while keeping the concentrations of $Ph_2P(O)H$ and phenylacetylene constant (Table S1).[26] The reaction order with respect to **1** was calculated (Figure 2a) and found to be 0.48, indicating that the reaction rate increases as the initial concentration of **1** increase. Next, initial rates were determined using different concentrations of $Ph_2P(O)H$ (0.5, 1.0, 1.5, and 2.0 M) while keeping the concentrations of **1** and phenylacetylene constant (Table S2, see Figure S167). The reaction order with respect to $Ph_2P(O)H$ was then calculated and found to be 0.25 (Figure 2b). Similarly, initial rates were determined using varying concentrations of phenylacetylene (0.4, 0.5, 0.6,

and 0.7 M) while keeping the concentrations of **1** and $Ph_2P(O)H$ constant (Table S3, see Figure S168). The reaction order with respect to phenylacetylene, calculated from the $\log_{10}(k_{obs})$ vs. $\log_{10}$(concentration of phenylacetylene) plot (Figure 2c), was found to be 0.45.

The rate equation of the reaction is; rate = $k[\mathbf{1}]^{0.48}$ $[Ph_2P(O)H]^{0.25}$ [phenylacetylene]$^{0.45}$

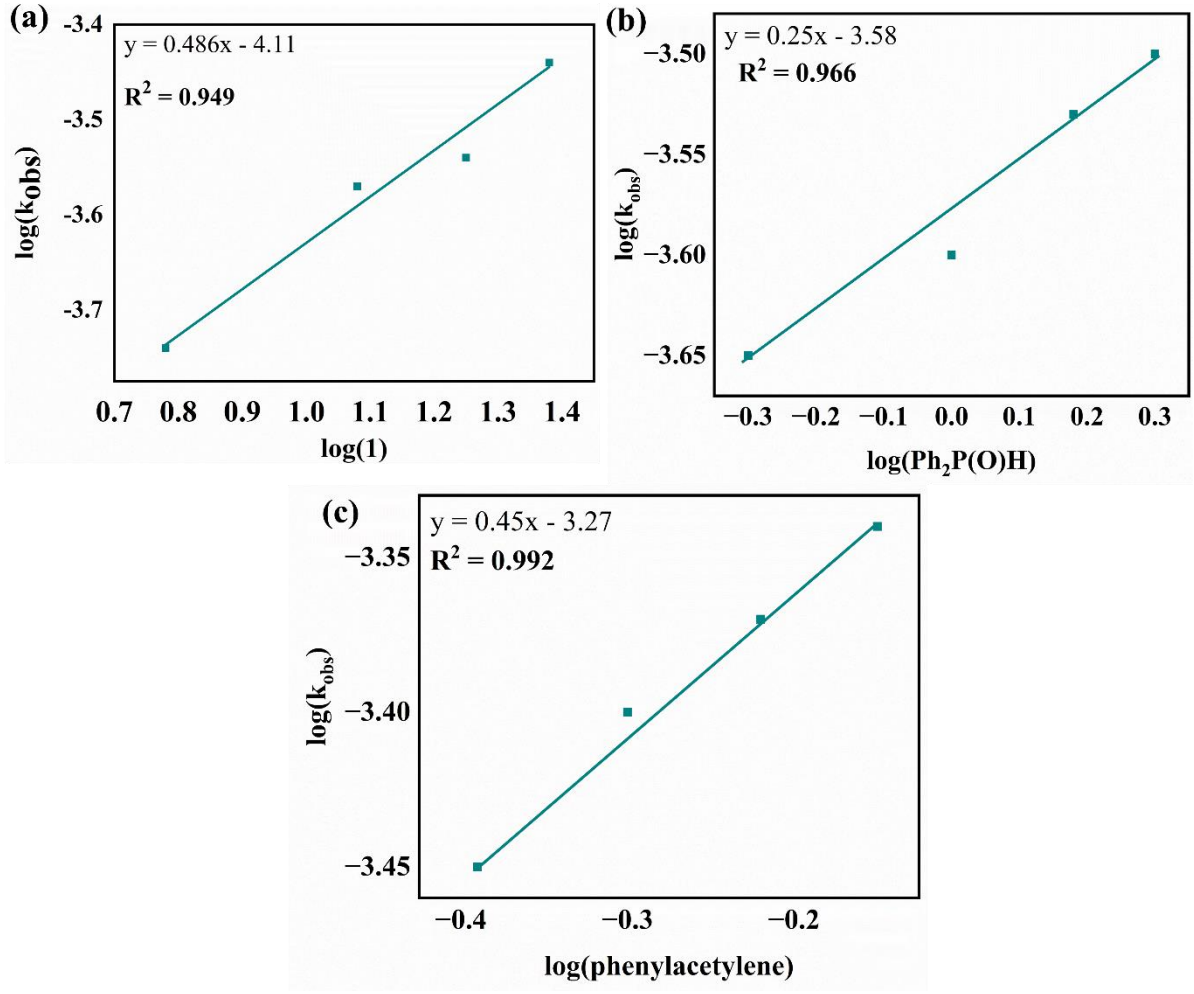


Figure 2. (a) Plot of $\log_{10}(k_{obs})$ vs $\log_{10}$(conc. of 1); (b) Plot of $\log_{10}(k_{obs})$ vs $\log_{10}$(conc. of $Ph_2P(O)H$); (c) Plot of $\log_{10}(k_{obs})$ vs $\log_{10}$(conc. of phenylacetylene).

Mechanistic Aspects

Experimental studies: To elucidate the mechanism of the hydrophosphinylation of alkynes, control experiments were conducted (Figure 3a). Initially, a stoichiometric reaction of 1:2 ratio between **1** and $Ph_2P(O)H$ was performed. Notably, this reaction yielded an Ph_2PO-coordinated Mg complex, bis(diiminate)-$MgOPPh_2$ (**1′**), as a P(III) species. The $^{31}P\{^1H\}$ NMR spectrum of

1′ displayed a peak at 88.6 ppm, Figure 3b, (see Figure S169 and S170), consistent with the values observed in Ph_2PO-bound magnesium complex[19] (87.6 ppm), calcium complex[27] (89.6 ppm), and lanthanum complex[28] (87.2 ppm). This observation is attributed to the tautomerization of $Ph_2P(O)H$ (P^V state) to the Ph_2POH (P^{III} state) prior to σ-bond metathesis.[29] Under reaction conditions, **1′** was further treated with phenylacetylene and diphenylphosphine oxide, resulting in the formation of desired product **4a**. However, to arrest the intermediate step i.e. the partial hydrophosphinylation of alkyne to alkene analogue **4a′**, we added 1:1 equiv. of $Ph_2P(O)H$ and phenylacetylene to a 5 mol% solution of **1** in C_6D_6. After 4 hours of reaction at room temperature, we observed a new $^{31}P\{^1H\}$ NMR signal at 27.6 ppm, (Figure 3b) and in ^1H NMR signals at 6.32 (dd) and 6.42 (dd) ppm were spotted. These NMR results along with mass data confirmed the formation of **4a′** and suggested the reaction to undergo via mono-hydrophosphinylation product (see Figure S171-173),[30] as addition of two more equiv. of $Ph_2P(O)H$ to the same reaction mixture and heating it at 80 °C for 12 hours led to the formation of 1,2-diphosphinylated product **4a**. The similar observation was also achieved with 4-ethylphenylacetylene (Figures S174-S176).

Computational Studies: The density functional theory (DFT) based calculations have been performed considering B3LYP and 6-31++G**/6-31G* level of theory, as implemented in Gaussian 09 package.[31-34] In the optimized structure of **1**, two monomeric units are connected via an oxygen atom, with the Mg centers present at 12.9 Å apart (see Figure S177). The highly exergonic free energy change (ΔG) for the sequential addition of 2 units of $Ph_2P(O)H$ at the Mg centers suggests both Mg centers are likewise active (see Figure S178). To reduce the computational cost, we have considered the single monomeric unit (**1^M**, M stands for monomer) for the mechanistic investigation of the hydrophosphinylation of phenylacetylene. The $Ph_2P(O)H$ reacts with pre-catalysts **1^M** to form the active catalyst **$1'^M$** (Figure 3c), and the step is found to be highly exergonic for both the cases. The calculated natural bond orbital (NBO)

charges show that the Mg center in the monomeric unit **1′ᴹ** and both the Mg centers in the dimeric unit **1′** are equivalent, making **1′ᴹ** representative of the overall activity of **1′** (see Figure S179).

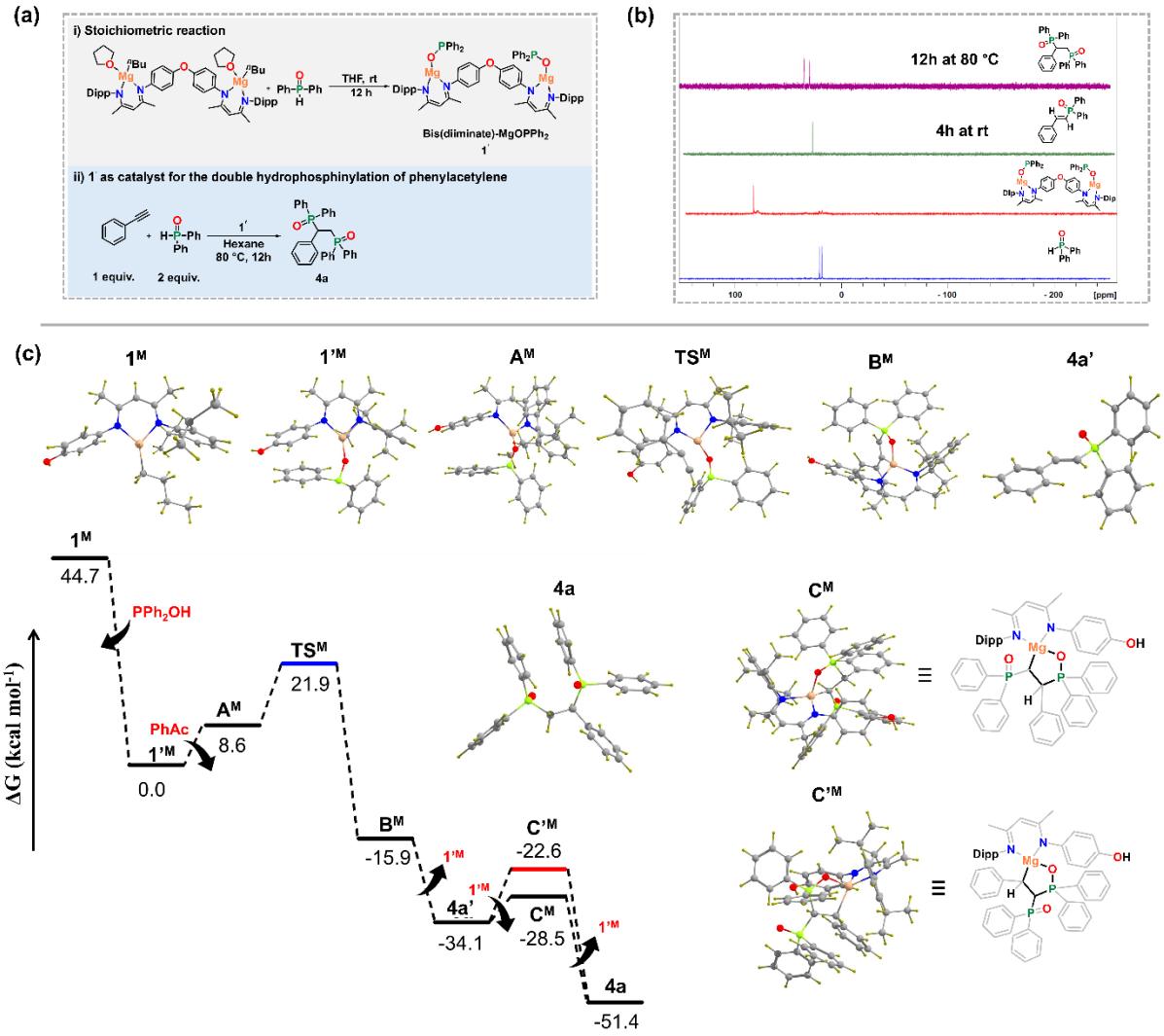


Figure 3. (a) Mechanistic experiments; (b) Stack ^{31}P NMR of diphenylphosphine oxide, **1′**, **4a′** and product **4a** (bottom to top respectively); (c) Reaction free energy profile diagram for the hydrophosphinylation of phenylacetylene. All the calculations were performed with B3LYP-D3/6-31++G**/6-31G* level of theory. Grey = C; Red = O; Green = P; Blue = N; Orange = Mg; Yellow = H.

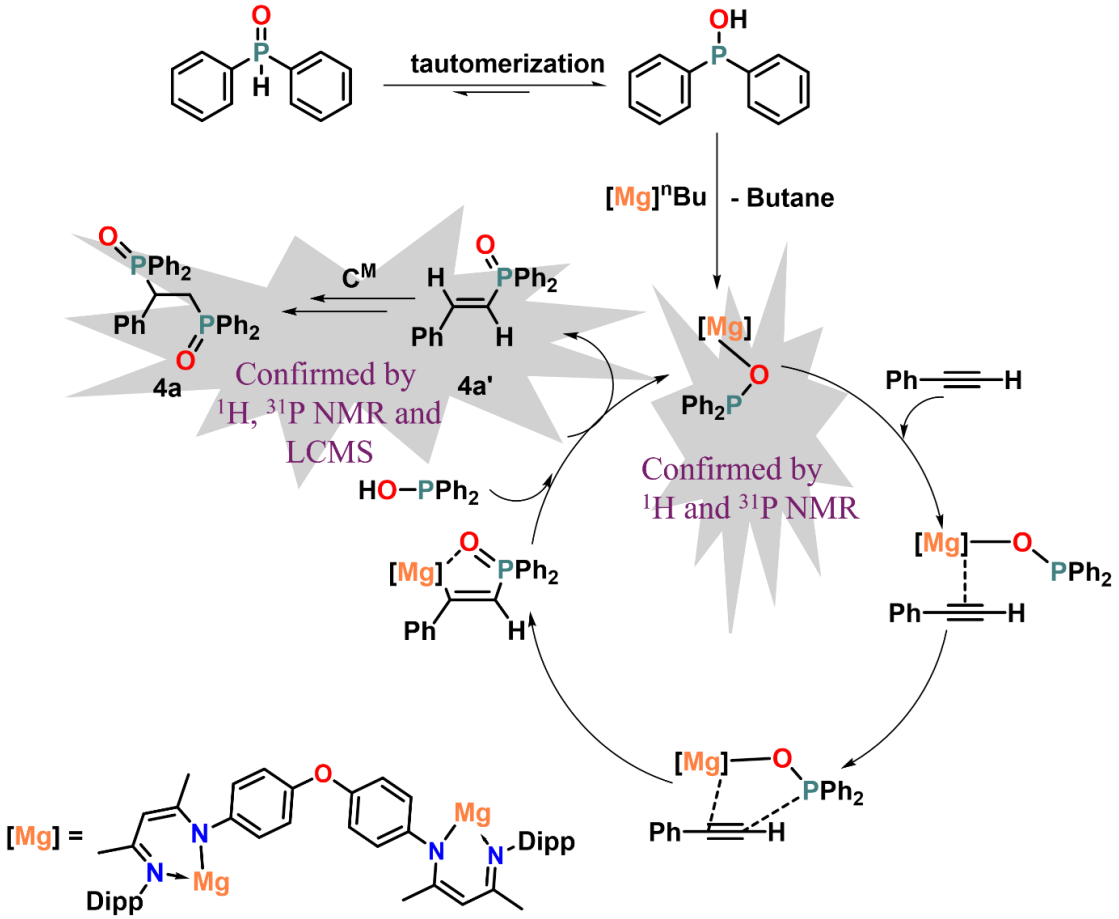
The overall reaction free energy diagram for the hydrophosphinylation of phenylacetylene considering **1′ᴹ** as an active catalyst is shown in Figure 3c. The reaction starts with the insertion of phenylacetylene, PhAc into **1′ᴹ**, resulting in intermediate **Aᴹ** with an endergonic energy

change of 8.6 kcal mol^{-1}. Subsequently, $\mathbf{A^M}$ converted into five-membered ring intermediate $\mathbf{B^M}$ through a transition state $\mathbf{TS^M}$, with an activation barrier of 21.9 kcal mol^{-1}. Afterwards, the breaking of the Mg–O bond occurs in $\mathbf{B^M}$, leading to the formation of an alkene intermediate **4a′** with highly exergonic energy change (–34.1 kcal mol^{-1}) and regeneration of the active catalyst $\mathbf{1'^M}$. Further, the alkene intermediate **4a′** reacts with $\mathbf{1'^M}$ to produce two isomers $\mathbf{C^M}$ and $\mathbf{C'^M}$ (Figure 3c). The formation of $\mathbf{C^M}$ is found to be energetically more favorable than $\mathbf{C'^M}$. The charge analysis of the **4a′** intermediate (see Figure S181) showed that the C2 carbon of **4a′** is more electropositive |-0.166 e| than that of C1 carbon |-0.625 e| and thus less reactive towards Mg centre leading to the formation of $\mathbf{C'^M}$. Finally, $\mathbf{C^M}$ reacts with $Ph_2P(O)H$ to form the desired product **4a**, namely, 1,2-diphosphinylated alkanes, with the regeneration of active catalyst $\mathbf{1'^M}$. The significantly exergonic overall free energy change, along with the moderate activation barrier, suggests that the reaction is highly feasible in the presence of the chosen catalyst.

Plausible Mechanism

Based on both experimental and theoretical findings, the proposed reaction mechanism for this study is illustrated in Scheme 3. Initially, diphenylphosphine oxide in its P(V) form tautomerizes to its P(III) counterpart, producing $Ph_2P(OH)$. This intermediate subsequently reacts with compound **1** to form a diphenylphosphinoyl-coordinated magnesium complex (**1'**). Instances of alkyne and alkene coordination to alkaline earth metals are limited because these metals exhibit lower Lewis acidity. In 2018, Hill, Maron, and colleagues demonstrated π overlap between the HOMOs of arenes and the valence *n*d orbitals of calcium in arene-calcium complexes. [35] In the case of magnesium, while the cationic species [BDI-Mg] can bind to an alkyne,[36] the coordination of an alkyne to a neutral Mg(II) complex is influenced by the nature of the attached ligand (Y in Mg-Y). The presence of the Ph_2PO group in complex **1'** imparts a δ+ charge to the magnesium (calculated |1.671 e|), enhancing its Lewis acidity compared to

complex **1** (calculated |1.493 e|). Subsequently, the [Mg]-$OPPh_2$ unit induces polarization of the π-electrons of the alkyne, facilitating the coordination of phenylacetylene to the magnesium



Scheme 3. Proposed mechanism for the hydrophosphinylation of alkynes using complex **1**.

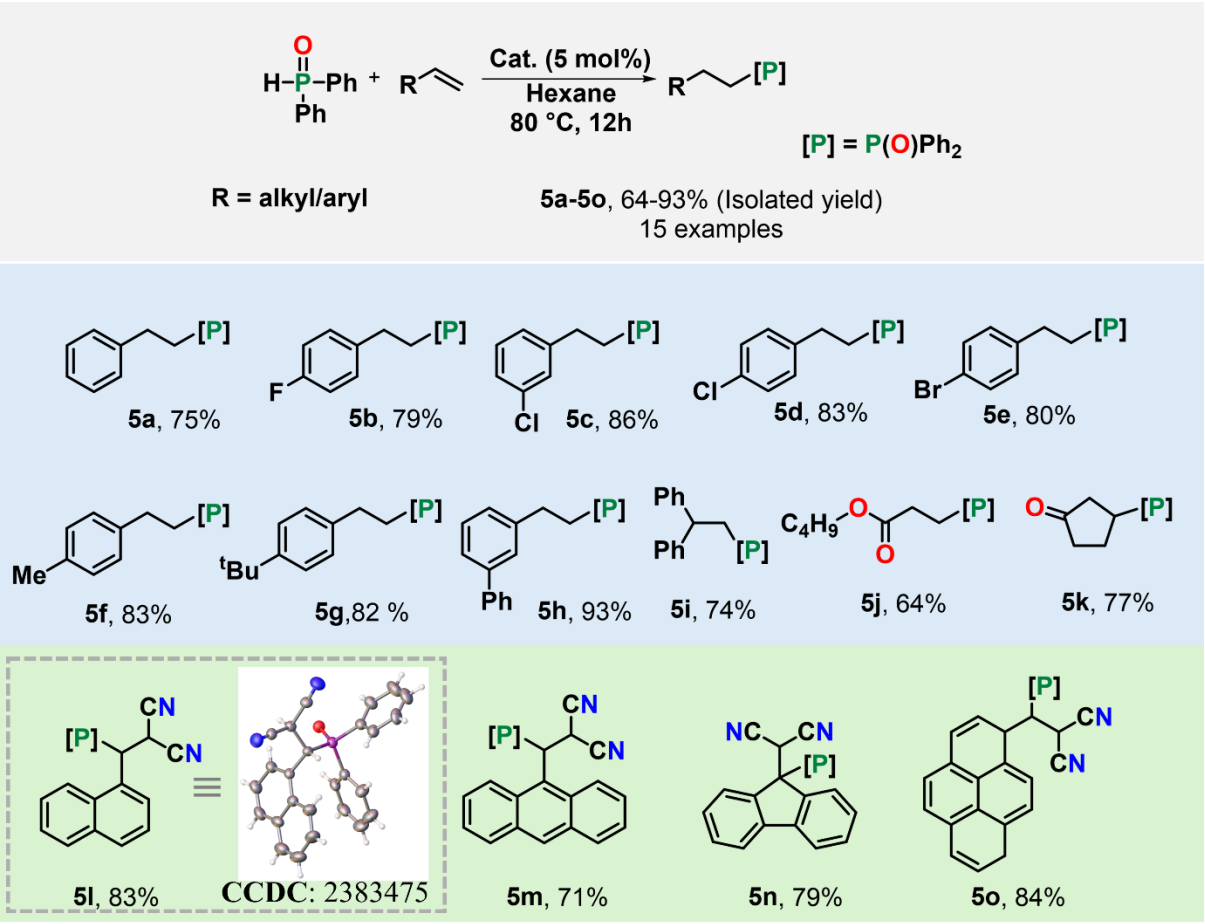
center of complex **1'** with an endergonic energy change of 8.6 kcal mol^{-1}. The semi-hydrogenation of alkynes using a magnesium-pincer complex demonstrated that the complex facilitates alkyne coordination to the magnesium center with a ΔG value of 9 kcal mol^{-1}.[37] Once the coordination of the alkyne to the magnesium center in complex **1'** is established, it transitions through a [3+2] transition state to form a five-membered intermediate. This intermediate is then protonated by diphenylphosphine oxide, achieving partial hydrophosphinylation of alkyne to yield alkenyl phosphine oxide (**4a′**). The newly formed alkene moiety (**4a′**) is sufficiently reactive to facilitate further addition of diphenylphosphine

oxide to complex **1'**, resulting in the formation of **4a** through another five-membered intermediate formation (see Figure 3c). The conversion of intermediate $\mathbf{C^M}$ to **4a** is energetically favourable, establishing **4a** as the thermodynamically controlled product. This is further supported by experimental findings, which indicate that the alkenyl phosphine oxide **4a′** is only obtained when the reaction is conducted at room temperature, using a 1:1 equivalent of $Ph_2P(O)H$ and phenylacetylene in a 5 mol% solution of complex **1**.

Hydrophosphinylation for alkenes

While there have been numerous studies on the transition metal-catalyzed hydrophosphinylation of unsaturated organic substrates, there has been only one report by Zheng and coworkers on the hydrophosphinylation of alkenes catalyzed by a Mg complex with 10 mol% of loading.[19] With the success of hydrophosphinylation of alkynes using **1**, we investigated the catalytic activity of **1** for the hydrophosphinylation of alkenes. The hydrophosphinylation of alkenes was carried out under the standard optimized conditions used for alkynes.

We treated various alkenes which led to the formation of corresponding β-arylphosphine oxides with 64-93% yields within 12 hours at 80 °C (**5a-5o**) (Scheme 4). In the hydrophosphinylation/hydrophosphination of alkenes, the addition of a phosphorus atom across the unsaturated bond can proceed via either a 1,2-addition or a 2,1-addition mechanism, yielding Markovnikov or anti-Markovnikov products, respectively.[38] In our study, we observed the formation of anti-Markovnikov products (**5a-5h**). With α,β-unsaturated alkenes or with activated alkenes, predominantly conjugated addition products were isolated (**5j-5o**).



Scheme 4. Hydrophosphinylation of alkenes catalyzed by Mg complex **1**[a].

[a]Reactions were conducted with alkene (0.24 mmol, 2.0 equiv.), diphenylphosphine oxide ($Ph_2P(O)H$) (0.48 mmol, 4.0 equiv.), complex **1** (5 mol %) in hexane, in a pressure/sealed tube at 80 °C for 12 h.

Conclusions

In summary, a series of bis(diiminate) magnesium complexes were synthesized and thoroughly characterized using spectroscopic studies and employed them in the catalytic hydrophosphinylation of alkynes and alkenes. Among the three complexes, complex **1** proved to be the most effective in the hydrophosphinylation of both alkenes and alkynes under mild conditions to afford high to excellent yields of organophosphorus compounds. In comparison, complex **3** exhibited moderate catalytic activity, while complex **2** showed significantly lower efficiency, highlighting the importance of ligand rigidity and electronic requirements on this

catalytic transformation. We have shown that stoichiometric reactions between complex **1** and $Ph_2P(O)H$ led to the formation of active species, **1′**, which subsequently reacted with alkynes to produce bis(phosphinylated) alkane derivatives, via mono(phosphinylated) alkene intermediates. Further, gram scale synthesis of bis(phosphinylated) alkanes was achieved by utilizing this method. All resulting derivatives and intermediates were characterized using ^{1}H and ^{31}P NMR spectroscopy and mass spectrometry. A theoretical study was conducted to provide insights into the mechanistic pathway, that truly predicts the stepwise formation of active catalyst **1′** and mono(phosphinylated) alkene via a five-membered cycle. These results highlighted by tuning the ligand framework could influence a subtle change in Lewis acidity at magnesium center. That facilitated a catalytic hydrophosphinylation reaction and showed that s-block metal catalysts are cementing their ground as an alternative to transition metal catalysts.

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Conflicts of interest

The authors declare no conflict of interest.

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ASSOCIATED CONTENT

Supporting Information

All experimental procedures, single crystal diffraction analysis, details of the DFT calculations, and additional data can be found in the Supporting Information. CCDC No. 2383475 contains the structure details of **5l**.

REFERENCES

1. (a) Magre, M.; Szewczyk, M.; Rueping, M. s-Block Catalyst for the Hydroboration of Unsaturated Bonds. *Chem. Rev.* **2022**, *122*, 8261-8312, DOI: 10.1020/acs.chemrev.1c00641; (b) Fohlmeister, L.; Stasch, A. Ring Shape Phosphinoamido-Magnesium-Hydride complex. *Chem.– Eur. J.* **2016**, *22*, 10235-10246,

DOI: 10.1002/chem.201601623; (c) Penafiel, J.; Maron, L.; Harder, S. Early Main Group Metal Catalysis: How Important is the Metal. *Angew. Chem., Int. Ed*. **2015**, *54*, 203-208, DOI: 10.1002/ange.201408814; (d) Wilkins, L. W.; Melen, R. Enantioselective Main Group Catalysis: Modern Catalysis for Organic Transformation. *Coord. Chem. Rev*. **2016**, *324*, 123-139, DOI: 10.1016/j.ccr.2016.07.011; (e) Shegavi, M. L.; Bose, S. K. Recent advances in the catalytic hydroboration of carbony compounds. *Catal. Sci. Technol*. **2019**, *9*, 3307-3336, DOI: 10.1039/C9CY00807A; (f) Weetman, C.; Inoue, S. The Road Travelled: After Main Group Elements as Transition Metals. *ChemCatChem*, **2018**, *10*, 4213-4228, DOI: 10.1002/cctc.201800963; (g) Pahar, S.; Kundu, G.; Sen, S. S. Cynosilylation by Compounds with Main Group Elements: An Odyssey. *ACS Omega*, **2020**, *5*, 25477-25484, DOI: 10.1021/acsomega.0c03293; (h) Langhals, L. Main Group Catalysis: Cationic Si(II) and Ge(II) Compounds as Catalyst in Organosilicon Chemistry. *Reactions*, **2021**, *2*, 442-456, DOI: 10.3390/reactions2040028

2. (a) Sarazin, Y.; Chapple, P. M.; Calcium, Strontium and Barium Complexes in Organic Synthesis. Parkin, G.; Meyer, K.; D. O'hare. Comprehensive Organometallic Chemistry IV (Fourth Edition), Elsevier, pp.104-192, **2022**, DOI: 10.1016/B978-0-12-820206-7.00069-X; (b) Sen, N.; Khan, S. Heavier Tetrylenes as Single Site Catalysts. *Chem.– Asian J.,* **2021**, *16*, 705-709, DOI: 10.1002/asia.202100038; (c) Ould, D.; Melen, R. L. Diazaphospholene and Diazaarsolene Derived Homogeneous Catalysis. *Chem.– Eur. J.*, **2020**, *26*, 9835-9845, DOI: 10.1002/chem.202001734; (d) Ansmann, N.; Johann, K.; Favresse, P.; Johann, T.; Fiedel, M.; Greb, L. Silicon-Catalyzed Depolymerization of Polyethers: Pushing Scope, Practicability and Mechanistic Understanding. *ChemCatChem*, **2024**, *16*, e202301615, DOI: 10.1002/cctc.202301615; (e) Ni, C.; Ma, X.; Yang, Z.; Roesky, H. W. Recent Advances in Aluminum Compounds for Catalysis. *Eur. J. Inorg. Chem*., **2022**, e202100929, DOI: 10.1002/ejic.202100929; (f) Lipshultz, J. M.; Li, G.; Radosevich, A. T.

Main Group Redox Catalysis of Organopnictogens: Vertical Periodic Trends and Emerging Opportunities in Group 15. *J. Am. Chem. Soc*., **2021**, *143*, 1699-1721, DOI: 10.1021/jacs.0c12816; (g) Akhtar, R.; Gaurav, K.; Khan, S. Applications of low-valent compounds with heavy group-14 elements. *Chem. Soc. Rev*., **2024**, *53*, 6150-6243, DOI: 10.1039/D4CS00101J; (h) Pramanik, M.; Guerzoni, M. G.; Richards, E.; Melen, R. Recent Advances in Asymmetric Catalysis Using p-Block Elements. *Angew. Chem., Int. Ed*., **2024**, *63*, e202316461, DOI: 10.1002/anie.202316461

3. (a) North, M.; Sustainable catalysis: With Non-endangered Metals; RSC Green Chemistry, Royal Society of Chemistry: Cambridge, U.K., **2015**; (b) Sarazin, Y.; Carpentier, J.-F. Calcium, Strontium and Barium Homogeneous Catalysts for Fine Chemicals Synthesis. *Chem. Rec.* **2016**, *16*, 2482-2505, DOI: 10.1002/tcr.201600067; (c) Hill, M. S.; Liptrot, D. J.; Weetman, C. Alkaline earths as main group reagents in molecular catalysis. *Chem. Soc. Rev.*, **2016**, *45*, 972-988, DOI: 10.1039/C5CS00880H; (d) Harder, S.; Early Main Group Metal Catalysis: Concepts and Reactions; John Wiley & Sons, Inc.: Newark, NJ, **2020**, DOI: 10.1002/9783527818020; (e) Fromm, K. M. Chemistry of alkaline earth metals: It is not all ionic and definitely not boring. *Coord. Chem. Rev.*, **2020**, *408*, 213193, DOI: 10.1016/j.ccr.2020.213193; (f) Hanusa, T. P. The lightest metals: Science and technology from lithium to calcium; EIC Books and John Wiley & Sons: Chichester, U.K., and Hoboken, NJ, **2015**
4. (a) Green, S. P.; Jones, C.; Stasch, A. Stable Magnesium(I) Compounds with Mg-Mg Bonds. *Science*, **2007**, *318*, 1754-1757; (b) Krieck, S.; Görls, H.; Yu, L.; Reiher, M.; Westerhausen, M. Stable "Inverse" Sandwich Complex with Unprecedented Organocalcium(I): Crystal Structures of $[(thf)_2Mg(Br)\text{-}C_6H_2\text{-}2,4,6\text{-}Ph_3]$ and $[(thf)_3Ca\{\mu\text{-}C_6H_3\text{-}1,3,5\text{-}Ph_3\}Ca(thf)_3]$ *J. Am. Chem. Soc.* **2009**, *131*, 2977-2985, DOI: 10.1021/ja808524y; (c) Jones, C. Dimeric magnesium(I) β-diketiminates: a new class of

quasi-universal reducing agent. *Nat. Rev. Chem.* **2017**, *1*, 0059, DOI: 10.1038/s41570-017-0059; (d) Jones, C. Open questions in low oxidation state group 2 chemistry. *Commun. Chem*. **2020**, *3*, 159, DOI: 10.1038/s42004-020-00408-8

5. (a) Harder, S. From Limestone to Catalysis: Application of Calcium Compounds as Homogeneous Catalysts. *Chem. Rev.*, **2010**, *110*, 3852-3876, DOI: 10.1021/cr9003659; (b) Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S., Procopiou, P. A. Heterofunctionalization catalysis with organometallic complexes of calcium, strontium and barium. *Proc. R. Soc. A*., **2010**, *466*, 927-963, DOI: 10.1098/rspa.2009.0558; (c) Arrowsmith, M.; Magnesium and Calcium Complexes in Homogeneous Catalysis. In Encyclopedia of Inorganic and Bioinorganic Chemistry, **2015**. DOI: 10.1002/9781119951438.eibc2299; (d) Rochat, R.; Lopez, M. J.; Tsurugi H.; Mashima, K. Recent Developments in Homogeneous Organomagnesium Catalysis. *ChemCatChem*, **2016**, *8*, 10-20, DOI: 10.1002/cctc.201500853; (e) Yang, D.; Wang, L.; Li, D.; Wang, R. Magnesium Catalysis in Asymmetric Synthesis. *Chem*. **2019**, *5*, 1108-1166, DOI: 10.1016/j.chempr.2019.02.002
6. (a) Zhang, X.; Emge, T. Z.; Hultzsch, K. C. Intramolecular Aminoalkene Hydroamination Catalyzed by Magnesium Complexes Containing Multidentate Phenoxyamine Ligands. *Organometallics*, **2010**, *29*, 5871-5877, DOI: 10.1021/om100675c; (b) Dunne, J. F.; Fulton, D. B.; Ellern, A.; Sadow, A. D. Concerted C−N and C−H Bond Formation in a Magnesium-Catalyzed Hydroamination. *J. Am. Chem. Soc.*, **2010**, *132*, 17680-17683, DOI: 10.1021/ja108881s; (c) Neal, S. R.; Ellern, A.; Sadow, A. D. Optically active, bulky tris(oxazolinyl)borato magnesium and calcium compounds for asymmetric hydroamination/cyclization. *J. Organomet. Chem*., **2011**, *696*, 228-234, DOI: 10.1016/j.jorganchem.2010.08.057
7. (a) Arrowsmith, M.; Hill, M. S.; Hadlington, T.; Kociok-Kçhn, G.; Weetman, C. Magnesium-Catalyzed Hydroboration of Pyridines. *Organometallics*, **2011**, *30*, 5556-

5559, DOI: 10.1021/om2008138; (b) Arrowsmith, M.; Hadlington, T. J.; Hill, M. S.; Kociok-Kçhn, G. Magnesium-catalysed hydroboration of aldehydes and ketones. *Chem. Commun*., **2012**, *48*, 4567-4569, DOI: 10.1039/c2cc30565h; (c) Arrowsmith, M.; Hill, M. S.; Kociok-Kçhn, G. Magnesium Catalysis of Imine Hydroboration. *Chem. Eur. J*., **2013**, *19*, 2776-2783, DOI: 10.1002/chem.201203190; (d) Intemann, J.; Lutz, M.; Harder, S. Multinuclear Magnesium Hydride Clusters: Selective Reduction and Catalytic Hydroboration of Pyridines. *Organometallics*, **2014**, *33*, 5722-5729, DOI: 10.1021/om500469h; (e) Mukherjee, D.; Ellern, A.; Sadow, A. D. Magnesium-catalyzed hydroboration of esters: evidence for a new zwitterionic mechanism. *Chem. Sci*., **2014**, *5*, 959-964, DOI: 10.1039/C3SC52793J

8. (a) Lampland, N. L.; Pindwal, A.; Neal, S. R.; Schlauderaff, S.; Ellern, A.; Sadow, A. D. Magnesium-catalyzed hydrosilylation of α,β-unsaturated esters. *Chem. Sci.* **2015**, *6*, 6901, DOI: 10.1039/C5SC02435H ; (b) Anker, M. D.; Hill, M. S.; Lowe J. P.; Mahon, M. F. Alkaline-Earth-Promoted CO Homologation and Reductive Catalysis. *Angew. Chem. Int. Ed.* **2015**, *54*, 10009, DOI: 10.1002/anie.201505851

9. (a) Liptrot, D. J.; Hill, M. S.; Mahon, M. F. Accessing the Single-Electron Manifold: Magnesium-mediated Hydrogen Release from Silanes. *Angew. Chem. Int. Ed.* **2014**, *53*, 6224-6227, DOI: 10.1002/anie.201403208; (b) Spielmann, J.; Bolte, M.; Harder, S. Synthesis and structure of a magnesium-amidoborane complex and its role in catalytic formation of a new bis-aminoborane ligand. *Chem. Commun*. **2009**, 6934-6936, DOI: 10.1039/b914979a; (c) Liptrot, D. J.; Hill, M. S.; Mahon, M. F.; MacDougall, D. J. Group 2 Promoted Hydrogen Release from $NMe_2H.BH_3$: Intermediates and Catalysis. *Chem. Eur. J.* **2010**, *16*, 8508-8515, DOI: 10.1002/chem.201000127; (d) Dunne, J. F.; Neal, S. R.; Engelkemier, J.; Ellern, A.; Sadow, A. D. Tris(oxazolinyl)boratomagnesium-Catalyzed

Cross-Dehydrocoupling of Organosilanes with Amines, Hydrazine, and Ammonia. *J. Am. Chem. Soc*. **2011**, *133*, 16782-16785, DOI: 10.1021/ja207641b

10. (a) Schwamm, R. J.; Day, B. M.; Mansfield, N. E.; Knowelden, W.; Hitchcock, P. B.; Coles, M. P. Catalytic bond forming reactions promoted by amidinate, guanidinate and phosphaguanidinate compounds of magnesium. *Dalton Trans*. **2014**, *43*, 14302-14314, DOI: 10.1039/C4DT01097C; (b) Schwamm, R. J.; Coles, M. P. Catalytic C-C Bond Formation Promoted by Organo- and Amidomagnesium(II) Compounds. *Organometallics* **2013**, *32*, 5277-5280, DOI: 10.1021/om400909e; (c) Zhang, W.-X.; Nishiura, M.; Hou, Z. Catalytic Addition of Terminal Alkynes to Carbodiimides by Half-Sandwich Rare Earth Metal Complexes. *J. Am. Chem. Soc.* **2005**, *127*, 16788-16789, DOI: 10.1021/ja0560027; (d) Yi, W.; Zhang, J.; Li, M.; Chen, Z.; Zhou, X. Synthesis, Structures, and Reactivity of Yttrium Alkyl and Alkynyl Complexes with Mixed Tp^{Me2}/Cp Ligands. *Inorg. Chem*. **2011**, *50*, 11813-11824, DOI: 10.1021/ic2019499; (e) Rochat, R.; Yamamoto, K.; Lopez, M. J.; Nagae, H.; Tsurugi, H.; Mashima, K. Organomagnesium-Catalyzed Isomerization of Terminal Alkynes to Allenes and Internal Alkynes. *Chem. Eur. J.* **2015**, *21*, 8112-8120, DOI: 10.1002/chem.201500179

11. (a) Quin, L. D.; A Guide to Organophosphorus Chemistry; Wiley Interscience: New York, **2000**; (b) Corbridge, D. E. C.; Phosphorus: Chemistry, Biochemistry and Technology, 6th ed.; CRC Press: London, **2013**, DOI: 10.1201/b12961; (c) Horsman, G. P.; Zechel, D. L. Phosphonate Biochemistry. *Chem. Rev.* **2017**, *117*, 5704-5783, DOI: 10.1021/acs.chemrev.6b00536; (d) Kukhar, V. P.; Hudson, H. R. Aminophosphonic and Aminophosphinic Acids: Chemistry and Biological Activity. Eds.; John Wiley & Sons: Chichester, **2000**; (e) Ordóñez, M.; Sayago, F. J.; Cativiela, C. Synthesis of quaternary α-aminophosphonic acids. *Tetrahedron*, **2012**, *68*, 6369-6412, DOI: 10.1016/j.tet.2012.05.008; (f) Kudzin, Z. H.; Kudzin, M. H.; Drabowicz, J.; Stevens, C. V.

Aminophosphonic Acids - Phosphorus Analogues of Natural Amino Acids.Part 1: Syntheses of α-aminophosphonic Acids. *Curr. Org. Chem*. **2011**, *15*, 2015-2071, DOI: 10.2174/138527211795703612; (g) Mucha, A.; Kafarski, P.; Berlicki, L. Remarkable Potential of the α-Aminophosphonate/Phosphinate Structural Motif in Medicinal Chemistry. *J. Med. Chem*. **2011**, *54*, 5955-5980, DOI: 10.1021/jm200587f; (h) Engel, R. Handbook of Organophosphorus Chemistry; New York, **1992**, DOI: 10.1201/9781482277241; (i) Hartley, F. R.; Patai, S. The Chemistry of Organophosphorus Compounds, Vol. 4; John Wiley & Sons: Chichester, **1996**; (j) Lam, K. H.; Gambri, R.; Yuen, M. C.; Kan, C. W.; Chan, P.; Xu, L.; Tang, W,; Chui, C. H. The preparation of 2,6-disubstituted pyridinyl phosphine oxides as novel anti-cancer agents. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 2266-2269, DOI: 10.1016/j.bmcl.2009.02.091; (k) Szajnman, S. H.; Ravaschino, E. L.; Docampo, R.; Rodriguez, J. B. Synthesis and biological evaluation of 1-amino-1,1-bisphosphonates derived from fatty acids against Trypanosoma cruzi targeting farnesyl pyrophosphate synthase. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 4685-4690, DOI: 10.1016/j.bmcl.2005.07.060

12. Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Phosphorus(III)Ligands in Homogeneous Catalysis: Design and Synthesis. Wiley, **2012**, DOI: 10.1002/9781118299715
13. Iaroshenko, V.; Organophosphorus Chemistry: From Molecules to Applications. Wiley-VCH, **2019**, DOI: 10.1002/9783527672240
14. Musina, E. I.; Balueva, A. S.; Karasik, A. A.; Phosphines: Preparation, Reactivity and Applications, Royal Society of Chemistry, **2019**, DOI: 10.1039/9781788016988-00001
15. (a) Bange, C. A.; Waterman, R. Challenges in Catalytic Hydrophosphination. *Chem. Eur. J.* **2016**, *22*, 12598-12605, DOI: 10.1002/chem.201602749; (b) Candy, M.; Rousseaux, S. A. L.; Román, A. C. S.; Szymczyk, M.; Kafarski, P.; Leclerc, E.; Vracken, E.; Campagne, J.-M. Palladium-Catalyzed Hydrophosphonylation of Alkenes with Dialkyl H-

Phosphonates. *Adv. Synth Catal*., **2014**, *356*, 2703-2708, DOI: 10.1002/adsc.201400190; (c) Han, L. B.; Zhang, C.; Yazawa, H.; Shimada, S. Efficient and Selective Nickel-Catalyzed Addition of H-P(O) and H-S Bonds to Alkynes. *J. Am. Chem. Soc.,* **2004**, *126*, 5080-5081, DOI: 10.1021/ja0494297; (d) Coudray, L.; Montchamp, J. L. Recent Developments in the Addition of Phosphinylidene-Containing Compounds to Unactivated Unsaturated Hydrocarbons: Phosphorus-Carbon Bond Formation by Hydrophosphinylation and Related Processes. *Eur. J. Org. Chem*. **2008**, *21*, 3601-3613, DOI: 10.1002/ejoc.200800331; (e) Han, L.-B.; Choi, N.; Tanaka, M. Oxidative Addition of $HP(O)PPh_2$ to Platinum(0) and Palladium(0) Complexes and Palladium-Catalyzed Regio- and Stereoselective Hydrophosphinylation of Alkynes. *Organometallics*, **1996**, *15*, 3259-3261, DOI: 10.1021/om960328u; (f) Han, L.-B.; Zhao, C.-Q.; Tanaka, M. Rhodium-Catalyzed Regio- and Stereoselective Addition of Diphenylphosphine Oxide to Alkynes. *J. Org. Chem.*, **2001**, *66*, 5929-5932, DOI: 10.1021/jo010337z

16. Harder, S.; Early Main Group Metal Catalysis, Wiley-VCH, **2020**, DOI: 10.1002/9783527818020
17. (a) Koshti, V.; Gaikwad, S.; Chikkali, S. H. Contemporary avenues in catalytic PH bond addition reaction: A case study of hydrophosphination. *Coord. Chem. Rev*. **2014**, *265*, 52-73, DOI: 10.1016/j.ccr.2014.01.006; (b) Novas, B. T.; Watermann, N. R. Metal-Catalyzed Hydrophosphination. *ChemCatChem*, **2022**, *14*, e202200988, DOI: 10.1002/cctc.202200988
18. Xu, Q.; Han, L. B. Metal-catalyzed additions of H-P(O) bonds to carbon-carbon unsaturated bonds. *J. Organomet. Chem*. **2011**, *696*, 130-140, DOI: 10.1016/j.jorganchem.2010.08.043

19. Zhang, L.; Bai, S.; Zheng, L. Magnesium-Catalyzed Regioselective Hydrophosphinylation of Alkenes with Diarylphosphine Oxides *Organometallics*, **2023**, *42*, 2262-2268, DOI: 10.1021/acs.organomet.3c00247

20. Fener, B. E.; Schüler, P.; Ueberschaar, N.; Bellstedt, P.; Görls, H.; Krieck, S.; Westerhausen, M. Scope and Limitations of the s-Block Metal-Mediated Pudovik Reaction. *Chem. Eur. J.* **2020**, *26*, 7235-7242, DOI: 10.1002/chem.201905565

21. (a) Gil-Negrete, J. M., Hevia, E. Main group bimetallic partnerships for cooperative catalysis. *Chem. Sci.* **2021**, *12*, 1982-1992, DOI: 10.1039/D0SC05116K; (b) Borys, A. M.; Hevia, E. Exploiting chemical cooperativity in main-group bimetallic catalysis. *Trends Chem*. **2021**, *3*, 803-806, DOI: 10.1016/j.trechm.2021.07.006

22. Platten, A. W. J.; Borys, A. M.; Hevia, E. Hydrophosphinylation of Styrenes Catalysed by Well-Defined s-Block Bimetallics. *ChemCatChem*, **2022**, *14*, e202101853, DOI: 10.1002/cctc.202101853

23. Parveen, D.; Yadav, R. K.; Mondal, B.; Dallon, M.; Sarazin, M.; Roy, D. K. Bis(diiminate)-based boron difluoro complexes: effective synthon for bis(borenium) cations. *Dalton Trans*., **2024**, *53*, 14139-14143, DOI: 10.1039/D4DT02050B

24. Rinke, P.; Görls, H.; Kretschmer, R. Calcium and Magnesium Bis(β-diketiminate) Complexes: Impact of the Alkylene Bridge on Schlenk-Type Rearrangements. *Inorg. Chem*., **2021**, *60*, 5310-5321, DOI: 10.1021/acs.inorgchem.1c00301

25. Piesik, D. F. -J.; Stadler, R.; Range, S.; Harder, S. Binuclear Magnesium, Calcium, and Zinc Complexes Based on Nitrogen–Nitrogen-Coupled Salicylaldiminate and β-Diketiminate Ligands. *Eur. J. Inorg. Chem*., **2009**, *2009*, 3569-3576, DOI: 10.1002/ejic.200900435

26. Arrowsmith, M.; Hadlington, T. J.; Hill, M.S.; Köhn, -K. G. Magnesium-catalysed hydroboration of aldehydes and ketones. *Chem. Commun.*, **2012**, *48*, 4567-4569, DOI: 10.1039/C2CC30565H

27. Mahon, M. F.; Robinson, T. P.; Hill, M. S. Calcium-centred phosphine oxide reactivity: P-C metathesis, reduction and P-P coupling. *Chem. Commun*. **2010**, *46*, 2498-2500, DOI: 10.1039/b923172b

28. Basiouny, M. M. I.; Dollard, D. A.; Schmidt, J. A. R. Regioselective Single and Double Hydrophosphination and Hydrophosphinylation of Unactivated Alkynes. *ACS Catal.* **2019**, *9*, 7143-7153, DOI: 10.1021/acscatal.9b01538

29. Waterman, R. σ-Bond Metathesis: A 30-Year Retrospective. *Organometallics*, **2013**, *32*, 7249-7263, DOI: 10.1021/om400760k

30. Li, J.; Gao, Z.; Guo, Y.; Liu, H.; Zhao, P.; Bi, X.; Shi, E.; Xiao, J. Copper-catalyzed stereo- and regioselective hydrophosphorylation of terminal alkynes: scope and mechanistic study. *RSC Adv*., **2022**, *12*, 18889-18896, DOI: 10.1039/D2RA02908A

31. Frisch, M. J. et al., Gaussian Revision D.01, Gaussian, Inc., Wallingford CT, **2013**

32. Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1972**, *56*, 2257-2261, DOI: 10.1063/1.1677527

33. Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, 270-283, DOI: 10.1063/1.448799

34. Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.*, **1985**, *82*, 299-310, DOI: 10.1063/1.448975

35. Garcia, L.; Anker, M. D.; Mahon, M. F.; Maron, L.; Hill, M. S. Coordination of arenes and phosphines by charge separated alkaline earth cations. *Dalton Trans.,* **2018**, *47*,12684-12693, DOI: 10.1039/C8DT03124J

36. Pahl, J.; Brand, S.; Elson, H.; Harder, S. Highly Lewis acidic cationic alkaline earth metal complexes. *Chem. Commun.,* **2018**, *54*, 8685-8688, DOI: 10.1039/C8CC04083D

37. Liang, Y.; Das, U. K.; Luo, J.; D-Posner, Y.; Avram, L.; Milstein, D. Magnesium Pincer Complexes and Their Applications in Catalytic Semihydrogenation of Alkynes and Hydrogenation of Alkenes: Evidence for Metal-Ligand Cooperation. *J. Am. Chem. Soc.* **2022**, *144*, 19115-19126, DOI: 10.1021/jacs.2c08491

38. (a) Bange, C. A.; Waterman, R. Challenges in Catalytic Hydrophosphination. *Chem. Eur. J*. **2016**, *22*, 12598-12605, DOI: 10.1002/chem.201602749; (b) Rosenberg, L. Mechanisms of Metal-Catalyzed Hydrophosphination of Alkenes and Alkynes. *ACS Catal*. **2013**, *3*, 2845-2855, DOI: 10.1021/cs400685c