Photocatalytic Hydrophosphination Using Calcium Precatalysts

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Dedicated to the memory of Ian Manners, an inspirational figure in catalysis in service of main group chemistry.

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Abstract: Hydrophosphination using calcium compounds as catalysts under irradiation is described as a foray into s-block photocatalysis. Transition-metal compounds have been highly successful hydrophosphination catalysts under photochemical conditions, utilizing substrates previously considered inaccessible. A calcium hydrophosphination precatalyst, Ca(nacnac)(THF)(N(SiMe$_3$)$_2$) (**1**, nacnac = HC[(C(Me)N-2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$), reported by Barrett and Hill, as well as the presumed intermediate, Ca(nacnac)(THF)(PPh$_2$) (**2**), and the Schlenk equilibrium product, Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (**3**) were screened under photochemical conditions with a range of unsaturated substrates including styrenic alkenes, Michael acceptors, and dienes with modest to excellent conversions, though unactivated alkenes were in accessible. All compounds exhibit enhanced catalysis under irradiation by LED-generated blue light. Nacnac-supported compounds generate radicals as evidenced by EPR spectroscopy and radical trapping reactions, whereas unsupported calcium compounds are EPR silent and appear to undergo insertion-based hydrophosphination akin to thermal reactions based. These results buttress the notion that photoactivation of π-basic ligands is a broad phenomenon, extending beyond the d-block, but like d-block metals, consideration of ancillary ligands is essential to avoid radical reactivity.

Introduction

Organophosphines are critical compounds in applications ranging from agriculture to materials, while being both important commodity and specialty chemicals.[1] Amid mounting concerns for phosphorus as a resource, efficiency in the synthesis of phosphorus-containing molecules is of key importance.[1b] Hydrophosphination is an atom-economical choice in organophosphine synthesis, but significant challenges remain for this transformation.[2] Prominent among these challenges are issues of substrate scope stemming from catalyst activity.[2a, b, d] For transition-metal catalysts, the most effective route to increasing activity and, therefore accessing more challenging substrates (e.g., unactivated alkenes) has been catalysis under irradiation.[2a, 3] Despite differing photochemical pathways,[3c, d, 4]activating an M–P bond by irradiation appears to be common across the d-block. It holds to reason that other metals may also be activated in this way, but this is an untested hypothesis.

S-block metals have been of consistent and increased interest for catalysis over the last two decades.[5] Hydrophosphination has been no stranger to these elements with examples of calcium,[6] potassium,[7] and sodium[7b, d, 8] being prominent among such studies.[2c] Efforts to use photocatalysis to enhance the activity of these metals appears to be absent from the literature. Many of these metals would be particularly attractive targets for enhanced reactivity due to their high natural abundance and low toxicity. The hypothesis of this study is that such activity is available to s-block elements. To test this hypothesis, a known hydrophosphination catalyst system was selected and comparisons between thermal and photolytic hydrophosphination were made.

Barret and Hill reported hydrophosphination catalysis using the β-diketiminato calcium compound Ca(nacnac)(THF)(N(SiMe$_3$)$_2$) (**1**, nacnac = HC[(C(Me)N-2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$) as a precursor and demonstrating that the proposed transient intermediate Ca(nacnac)(THF)(PPh$_2$) (**2**) is viable in the catalysis.[6c] The Schlenk equilibrium product, Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (**3**) was also demonstrated to be viable in catalysis.[9] These compounds were selected for the study due to their known activity. Reported catalysis was conducted at elevated temperatures, while photocatalysis can be conducted at ambient temperatures. The comparison in this study is at ambient temperature, and results show that all three calcium compounds exhibit enhanced activity under irradiation. The compounds diverge based on the ancillary ligand, though. Compounds supported by the β-diketiminate ligand appear to initiate radical reactivity, consistent with prior reports of triamidoamine-supported titanium and zirconocene compounds under irradiation as well as thermal reactivity of iron β-diketiminate compounds.[3d, 10] The bisamide derivative **3** gives no evidence of radical chemistry and exhibits similar mechanistic features to the thermal reactivity, suggesting insertion based hydrophosphination. Overall, photocatalysis is a viable way to improve activity in the s-block, but attention to coordination environment is needed to retain closed-shell reactivity.

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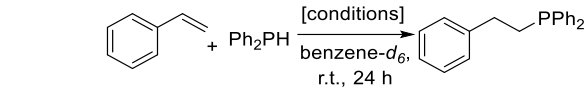
Results and Discussion

Initial screening for this study sought to identify enhanced catalysis under photochemical conditions, and ambient temperature was selected due to the lower energetic input, despite the difference in conditions from prior reports with these compounds.[6c] A test reaction of equimolar styrene and Ph_2PH in the presence of 5 mol % of each compound over 24 h was used to compare the impact of light. Blue light via LED was selected for convenience and safety factors. The three compounds in this study all showed significant enhancement in conversion upon irradiation as compared to reactions in the dark and under ambient light (Figure 1). The initial hypothesis of this study, that photocatalytic hydrophosphination is available to s-block metals, was borne out, but the nature of the photochemistry was not yet understood. Efforts to understand the catalysis initiated with spectroscopy study of the catalysts and reaction mixtures.



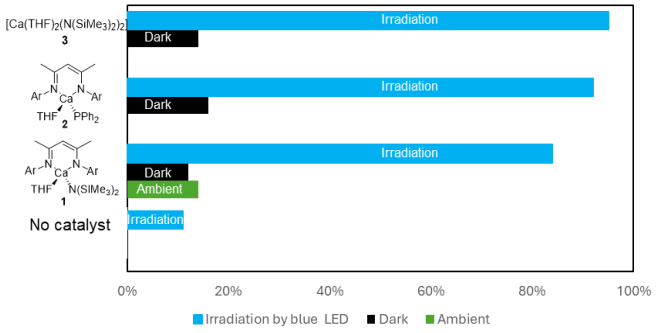
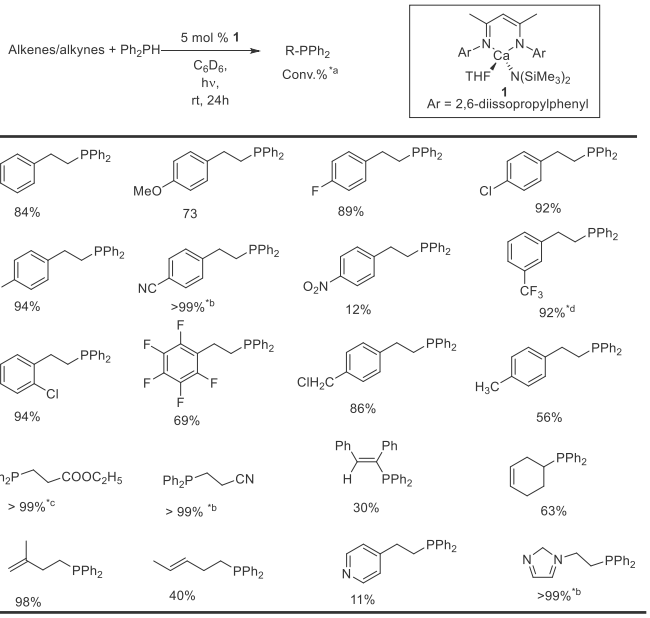


Figure 1 Hydrophosphination of styrene with Ph_2PH in benzene-d_6 to form $PhCH_2CH_2PPh_2$ under direct irradiation (blue) versus ambient light (green) and control reactions in the dark (black) with compounds **1**, **2**, and **3**, respectively (Ar = 2,6-diisopropylphenyl).

The UV-vis spectra of catalysts **1** and **2**, collected in in benzene solution for consistency with catalytic runs, exhibited lowest energy absorption bands at 321 nm and 325 nm, respectively, with no measurable absorptions in the visible region (see Supporting Information). However, the reaction mixture of equimolar styrene and Ph_2PH with either compound in benzene solution displayed a pronounced red shift in the lowest energy transition, with new absorption bands trailing into the visible, consistent with visual observations of reactions. Despite the limited overlap of the absorbance band, the study was continued with blue LED irradiation with the understanding that wavelength is a condition that can be optimized.

Compound **1** was applied to a range of substrates, including styrene derivatives, unactivated alkenes, dienes, Michael acceptors, and alkynes. Standard conditions consisted of equimolar amounts of alkene and Ph_2PH with 5 mol % of **1** in benzene-d_6 solution, and irradiation with a 9-W blue LED at ambient temperature, with reaction progress monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy (Table 1). Conversions among styrene substrates were greatest for those featuring electron withdrawing substituents. Reactions of dienes proceeded from modest to excellent conversion under standard conditions, and minimal amounts (≤5%) of 1,4-addition products were observed with conjugated diene substrates. Alkyne substrates gave only modest conversions, where the reaction of phenylacetylene gave 10% conversion (see Supporting Information), which maybe a consequence of substrate inhibition.[11] The hydrophosphination of 1-vinyl imidazole and acrylonitrile showed nearly quantitative conversion without irradiation, consistent with conjugate addition and the higher intrinsic reactivity of these substrates. Overall, though, conversions here are modest compared to many literature reports of metal-catalyzed hydrophosphination.[2c]

Table 1 Substrate scope for compound **1** as precatalyst



[a]The conversions were determined by ^1H NMR spectroscopy with trimethoxybenzene as the internal standard. [b]No direct irradiation. [c]18 h irradiation. [d]14 h irradiation.

There are outliers to the reactivity trends. Unexpectedly little conversion was observed in the case of 4-nitrostyrene and 2-vinylpyridine as substrates under standard conditions. Likewise, the reaction of a different activated alkene, ethyl acrylate, required irradiation to proceed. This reaction was qualitative faster than styrenic substrates, complete in less than 18 h, but the need for irradiation is inconsistent with conjugate addition reactions seen with other metal catalysts utilizing acrylate substates.[3c] It was unsurprising, though disappointing, that a broad set of substrates had no significant conversion including, 1-hexene, 1-octene, trans-stilbene, 2,3-dimethyl 2-butene, α-methyl styrene, β-methyl styrene, β-bromo styrene, α-methyl (4-trifluoromethyl) styrene, and cyclohexene. Limited reactivity with these substrates was not unexpected as unactivated alkenes and those with greater steric

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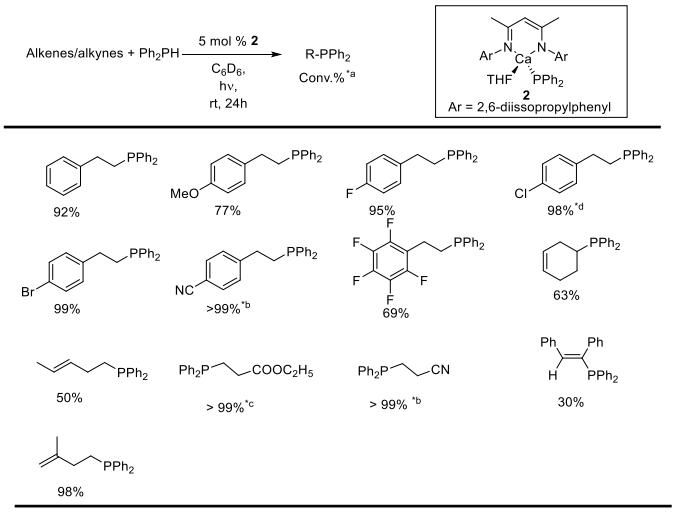
profiles, very few catalysts can access them.[2a, 12] Nevertheless, outliers prompted a deeper consideration of mechanism.

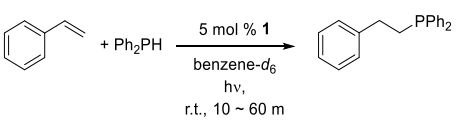
To understand the system, compound **2**, a known derivative and proposed intermediate in the catalysis,[6c] was prepared and tested. Screening of compound **2** at 5 mol % loading under standard conditions afforded the same conversions as did compound **1** (Table 2). This observation stands as evidence that compound **2** is catalytically viable, whether or not it is an intermediate.

Table 2 Substrate scope for compound **2** as precatalyst



[a] The conversions were determined by ^{1}H NMR spectroscopy with trimethoxybenzene as the internal standard. [b] No blue LED was applied. [c] 18 h under blue LED irradiation. [d] 20 h under blue LED irradiation.

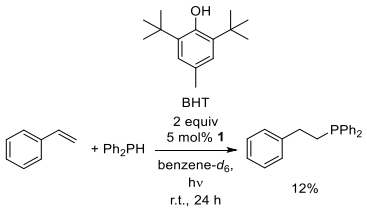
As an initial probe of mechanism, a competitive Hammett analysis was performed using substituted styrene substrate. In these experiments, 0.5 mmol each of styrene and para-substituted styrene with 5 mol % of **1** in benzene-d_6 solution were treated with 0.5 mmol of Ph_2PH under blue LED irradiation at ambient temperature. Relative conversions were determined after 1 h by ^{1}H NMR spectroscopy. A small but positive slope (ρ = 0.94) was measured. This positive ρ value implies a mechanistic preference involving a negative charge in the transition state, consistent with the empirically observed electronic effects (Table 1).



Scheme 1 Catalytic hydrophosphination for kinetic studies.

An Eyring analysis based on rate measurements was also performed on the parent reaction of styrene and diphenylphosphine with compound **1**. The activation enthalpy value ($\Delta H^{\ddagger}$ = 9.57 kcal mol^{-1}) is relatively low, consistent with the modest energy of a P–H bond.[13] The negative activation entropy ($\Delta S^{\ddagger}$ = –47.03 e.u.) demonstrates an ordered assembly in the transition state, and it also may support a radical or ion-pair intermediate.[14] Empirically these data are consistent with the notion that thermal catalysis is required in the absence of light given the free energy value ($\Delta G^{\ddagger}$ = 23.6 kcal mol^{-1}).[15] The combination a relatively low activation barrier and ordered transition state are characteristic of several transformations and more information is needed for an mechanistic proposal.[16]

These experiments did not provide significant mechanistic understanding, but a simple inhibition reaction did. In reaction of styrene and Ph_2PH under standard conditions (vide supra), 2 equiv. of BHT (2,6-di-tert-butyl-4-methylphenol), a known radical inhibitor (Scheme 2),[17] was added at the beginning of a standard reaction. Despite a 24 h period of irradiation, only 12% conversion to product was measured. Such inhibition by BHT is consistent with a radical-based mechanism and pointed toward a need for better data to fully understand the system.[18]



Scheme 2 The radical trap reaction with BHT under standard reaction conditions.

A robust and simple approach for detecting radical activity in photocatalytic reactions is EPR spectroscopy[10a, 19] Control EPR spectra of **1** in benzene solution at ambient temperature does not show any signal before irradiation or after irradiation for 1 h. In catalytic mixtures an EPR signal was measured after irradiation in the visible for 1 h. Assignment of the EPR data is on-going, but noticeable hyperfine coupling indicates significant interactions of the unpaired electron, likely around the ancillary ligand. An identical EPR experiment with compound **2** as precatalyst also gave signal after 1 h irradiation, though the intensity is relatively low in comparison.[10b, 20]

These EPR data indicate that radical chemistry is likely the result of irradiation of the catalytic reactions. Interestingly, an example of observed radical but an inability to fully identify radical reactivity was reported.[21] The BHT inhibition reactions suggest that the photo-induced radicals are likely initiating hydrophosphination and help to clarify that this is photo-initiated radical hydrophosphination.

In the course of these experiments, a deuterium labeling study was performed on the model reaction using **1** (Scheme 3). Styrene was treated with 1 equivalent of diphenylphosphine-d_1 (80% deuteration) and 5 mol % of **1** under irradiation and

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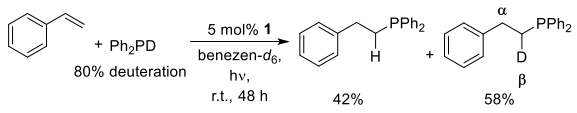
monitored by ^{1}H, ^{2}H, $^{31}P\{^{1}H\}$, $^{31}P\{^{1}H\}$-^{1}H HSQC, HMBC, ^{13}C-^{1}H HSQC, and HMBC NMR spectroscopy. After 48 h, 48% conversion to product was measured, qualitative evidence for a non-trivial kinetic isotope effect. Residual proteo phenylphosphine was fully consumed and represents 42% of the measured protonated product. The balance of the product (58%) contained a single deuterium. Analysis of the NMR spectra (see Supporting Information) confirmed exclusive deuteration at the carbon adjacent to the diphenylphosphine substituent, or a formal 1,1-addition to styrene. Other 1,1-addition reactions in hydrophosphination are known, but this reaction has only been observed with alkyne substates.[7d]

The observed selectivity suggests that the reaction is a concerted process. Kinetic data and the large, negative $\Delta S^{\ddagger}$ value appear to support a highly ordered transition state that would allow for this type of selectivity. Nevertheless, the results from the deuterium labeling experiments are truly surprising, particularly for a radical initiation pathway. Further study is required for clear insights into the underlying reaction pathway to afford the products of the deuterium labeling reaction. Understanding the selectivity may be particularly informative results because the limited examples Markovnikov selectivity in metal-catalyzed hydrophosphination has been proposed from an open-shell iron compounds.[10b, 22]

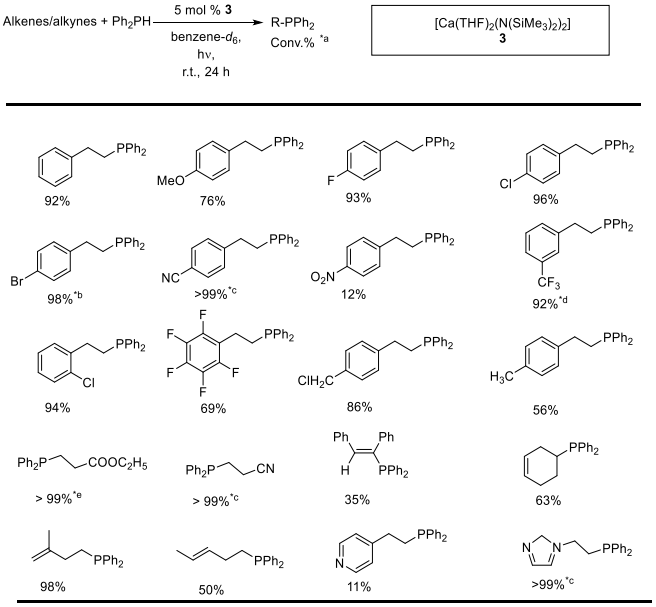


Scheme 3 Deuterium labeling reaction, percent conversions of isotopomers are of the total hydrophosphination product (48% total conversion).

The radical reactivity associated with compounds **1** and **2** is interesting but does not test the core hypothesis regarding photoactivation for metal-based catalysis. A precursor to **1**, compound **3**, is also known to be an active precatalyst for this transformation and lacks the non-innocent β-diketiminate ligand.[6c, 20] These compounds also showed enhanced catalysis upon irradiation, but EPR spectra of irradiated catalysis runs failed to give signal (see Supporting Information). Like transition-metal compounds, s-block metals are capable of photocatalytic hydrophosphination via an apparent closed-shell pathway.

With a closed-shell s-block photocatalyst in hand, a screening of substrates was undertaken using **3** as pre-catalyst. Results are consistent with the screening reaction (Figure 1) in which modest to excellent conversions can be obtained under standard conditions for most activated and styrenic substrates (Table 3). There are still peculiarities associated with some substrates compared to norms established in prior reports.

Table 3 Substrate scope

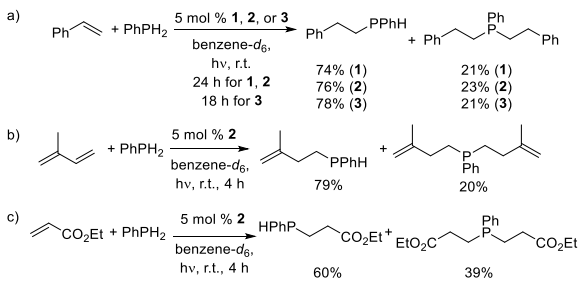


[a]The conversions were determined by ^{1}H NMR spectroscopy with trimethoxybenzene as the internal standard. [b]20 h under irradiation. [c]No irradiation. [d]14 h irradiation. [e]18 h irradiation.

Hydrophosphination catalysis with compound **3** has some significant limits, and unactivated alkenes as well as sterically encumbered substrates are virtually untouched. Less encumbered substrates were not a challenge as shown by nearly identical, high conversions for both 2-chlorostyrene and 4-chlorostyrene. Alkyne substrates are subject to hydrophosphination to limited extent with **3**, and like compounds **1** and **2**, 4-nitrostyrene, yield was scarcely converted under standard conditions. These lower conversions may represent unfavorable catalyst interactions with substrate.

A significant limitation to this compound was solubility in benzene solution. Yellow precipitate was observed in catalytic reactions, a byproduct likely to be the polymeric calcium phosphide $[Ca(PPh_2)(S)_x]_y$ (S = THF, Ph_2PH),[6c, 9] which may diminish activity by lowering effective catalyst concentration.

A simple extension of these two categories precatalysts was undertaken with primary phosphine. Reaction of styrene with equimolar phenylphosphine and 5 mol% of each of the three catalysts under standard conditions gave high conversions (Scheme 4a). This is likely due to the less sterically encumbered phosphine substrate. The best of the three was compound **3**, achieving quantitative yield in less time.[23] In all cases, the double P–H activation product was a competitive by product.[10a]



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Scheme 4 Hydrophosphination of styrene, isoprene and ethyl acrylate with $PhPH_2$ using compounds **1**, **2**, and **3**. Conversions are measured by $^{31}P\{^1H\}$ NMR spectroscopy, reflecting the ratio of products under limiting alkene.

Additionally, hydrophosphination of ethyl acrylate and isoprene with $PhPH_2$ using all three compounds showed good conversions in short reaction times (Scheme 4b and c). Though some unidentified peaks appeared in the $^{31}P\{^1H\}$ NMR spectra, the ^1H NMR spectra confirmed that both ethyl acrylate and isoprene were fully consumed within 4 h in all cases, forming a mixture of the single and double P–H bond activation products.

Conclusion

This study demonstrates that calcium-based compounds can engage in photocatalytic hydrophosphination under mild reaction conditions. Mechanistic investigation revealed a radical based catalytic reaction for catalysts **1** and **2**, wherein blue LED irradiation drives the activation of calcium-substrate complexes. The observation of radical signals via EPR spectroscopy under catalytic conditions and the dramatic inhibition of product formation upon a radical scavenger addition confirms radical hydrophosphination. In the case of **3**, no evidence for radical chemistry is observed, and these reaction appear to mimic the reported, insertion-based thermal catalysis.[6c] Comparative studies of the three catalysts reveal the critical impact of ligand architecture and ancillary stabilization on catalytic efficiency, with **3** outperforming its analogs under identical conditions, consistent with a different mechanistic pathway. Overall, this work supports the continued use of photolysis as a general method to enhance hydrophosphination catalysis, including the s block, with the caveat that ancillary ligand choice is a key factor.

Supporting Information

Experimental procedures and full spectroscopic data. Original data from the study is archived at www.uvm.edu/~waterman.

Acknowledgements

This work was supported by the U. S. National Science Foundation through awards CHE-2348198 and TI-2329625.

Keywords: hydrophosphination • calcium • photocatalysis • radical • phosphine

References:

[1] a) C. Alewell, B. Ringeval, C. Ballabio, D. A. Robinson, P. Panagos and P. Borrelli, *Nat. Commun.,* **2020**, *11*, 4546; b) C. E. Nedelciu, K. V. Ragnarsdottir, P. Schlyter and I. Stjernquist, *Glob. Food. Secure-AGR,.* **2020**, *26*, 100426; c) H. Yu, H. Yang, E. Shi and W. Tang, *Med. Drug Discov.* **2020**, *8*, 100063; d) J. C. Slootweg, *Angew. Chem. Int. Ed.* **2018**, *57*, 6386-6388; e) C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313-348; f) D. E. C. Corbridge, *Phosphorus: Chemistry, Biochemistry and Technology, Sixth Edition*, CRC Press, **2013**, p.

[2] a) C. A. Bange and R. Waterman, *Chem. Eur. J.* **2016**, *22*, 12598-12605; b) S. Lau, T. M. Hood and R. L. Webster, *ACS Catal.* **2022**, *12*, 10939-10949; c) B. Novas and R. Waterman, *Metal-Catalyzed Hydrophosphination*, **2022**, p; d) L. Rosenberg, *ACS Catal.* **2013**, *3*, 2845-2855; e) R. G. Belli, J. Yang, E. N. Bahena, R. McDonald and L. Rosenberg, *ACS Catal.* **2022**, *12*, 5247-5262; f) D. S. Glueck, *J. Org. Chem* **2020**, *85*, 14276-14285; g) D. K. Wicht, I. V. Kourkine, B. M. Lew, J. M. Nthenge and D. S. Glueck, *J. Am. Chem. Soc.* **1997**, *119*, 5039-5040; h) C. Scriban, D. S. Glueck, L. N. Zakharov, W. S. Kassel, A. G. DiPasquale, J. A. Golen and A. L. Rheingold, *Organometallics* **2006**, *25*, 5757-5767; i) D. S. Glueck, *J. Org. Chem.* **2020**, *85*, 14276-14285; j) D. Glueck, *ChemInform* **2011**, *42*; k) D. S. Glueck, *Chem. Eur. J.* **2008**, *14*, 7108-7117.

[3] a) R. Waterman, *Acc. Chem. Res.* **2019**, 52, 2361-2369; b) M. B. Reuter, D. M. Seth, D. R. Javier-Jiménez, E. J. Finfer, E. A. Beretta and R. Waterman, Chem. Commun. **2023**, 59, 1258-1273; c) S. G. Dannenberg, D. M. Seth, Jr., E. J. Finfer and R. Waterman, *ACS Catal.* **2023**, 13, 550-562; d) C. A. Bange, M. A. Conger, B. T. Novas, E. R. Young, M. D. Liptak and R. Waterman, *ACS Catal.* **2018**, 8, 6230-6238.

[4] B. Novas, C. Bange and R. Waterman, *Eur. J. Inorg. Chem*. **2018**, 2019.

[5] M. Magre, M. Szewczyk and M. Rueping, *Chem. Rev.* **2022**, *122*, 8261-8312.

[6] a) Y. Sarazin and J. F. Carpentier, *Chem Rec* **2016**, *16*, 2482-2505; b) I. V. Lapshin, A. V. Cherkasov and A. A. Trifonov, *Organometallics* **2023**, *42*, 2531-2540; c) M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. B. Hitchcock and P. A. Procopiou, *Organometallics* **2007**, *26*, 2953-2956; d) M. R. Crimmin, I. J. Casely and M. S. Hill, *J. Am. Chem. Soc.* **2005**, *127*, 2042-2043; e) T. M. A. Al-Shboul, H. Görls and M. Westerhausen, *Inorg. Chem. Commun.* **2008**, *11*, 1419-1421; f) B. J. Ward and P. A. Hunt, *ACS Catal.* **2017**, *7*, 459-468; g) B. Liu, T. Roisnel, J.-F. Carpentier and Y. Sarazin, *Angew. Chem. Int. Ed.* **2012**, *51*, 4943-4946; h) S.-C. Roşca, T. Roisnel, V. Dorcet, J.-F. Carpentier and Y. Sarazin, *Organometallics* **2014**, *33*, 5630-5642; i) S. Anga, J.-F. Carpentier, T. K. Panda, T. Roisnel and Y. Sarazin, *RSC Advances* **2016**, *6*, 57835-57843; j) A. O. Tolpygin, A. V. Cherkasov, G. K. Fukin, T. A. Kovylina, K. A. Lyssenko and A. A. Trifonov, *Eur. J. Inorg. Chem.* **2019**, *2019*, 4289-4296.

[7] a) S. M. Härling, B. E. Fener, S. Krieck, H. Görls and M. Westerhausen, *Organometallics* **2018**, 37, 4380-4386; b) M. T. Whitelaw, S. Banerjee, A. R. Kennedy, A. van Teijlingen, T. Tuttle and R. E. Mulvey, *Cell Rep. Phys. Sci.* **2022**, 3, 100942; c) T. Bunlaksananusorn and P. Knochel, *Tetrahedron Lett* **2002**, 43, 5817-5819; d) N. T. Coles, M. F. Mahon and R. L. Webster, *Chem. Commun.* **2018**, 54, 10443-10446.

[8] a) S. Asako, Chem Catalysis 2022, 2, 1529-1531; b) E. J. Finfer and R. Waterman, *Green Chem.* **2025**, 27, 432-437.

[9] M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. B. Hitchcock and P. A. Procopiou, *Organometallics* **2008**, *27*, 497-499.

[10] a) D. M. Seth, Jr. and R. Waterman, *Organometallics* **2023**, 42, 1213-1219; b) M. Espinal-Viguri, A. K. King, J. P. Lowe, M. F. Mahon and R. L. Webster, *ACS Catal.* **2016**, 6, 7892-7897.

[11] A. J. Roering, S. E. Leshinski, S. M. Chan, T. Shalumova, S. N. MacMillan, J. M. Tanski and R. Waterman, *Organometallics* **2010**, 29, 2557-2565.

[12] S. G. Dannenberg and R. Waterman, *Chem. Commun.* **2020**, 56, 14219-14222.

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[13] a) L. Coudray and J. L. Montchamp, *Eur. J. Org. Chem.* **2008**, 3601-3613; b) K. Balasubramanian, Y. S. Chung and W. S. Glaunsinger, The *J. Chem. Phys*. **1993**, 98, 8859-8869.

[14] J. Sobek, R. Martschke and H. Fischer, *J. Am. Chem. Soc.* **2001**, 123, 2849-2857.

[15] A. F. Tuck, *Entropy* **2019**, 21, 1044.

[16] L. L. Schaleger and F. A. Long in Entropies of Activation and Mechanisms of Reactions in Solution, Vol. 1 (Ed. V. Gold), Academic Press, 1963, pp. 1-33.

[17] S. Fujisawa, Y. Kadoma and I. Yokoe, *Chem. Phys. Lipids* **2004**, 130, 189-195.

[18] Y. Huo, H. Zhu and X. He, ACS Omega 2022, 7, 18552-18568.

[19] D. R. Javier-Jiménez, B. T. Novas and R. Waterman, *Eur. J. Inorg. Chem.* **2023**, 26, e202300341.

[20] M. M. Khusniyarov , E. Bill, T. Weyhermüller, E. Bothe and K. Wieghardt, *Angew. Chem. Int. Ed.* **2011**, 50, 1652-1655.

[21] M. B. Reuter, D. R. Javier-Jiménez, C. E. Bushey and R. Waterman, *Chem. Eur. J.* **2023**, 29, e202302618.

[22] L. Routaboul, F. Toulgoat, J. Gatignol, J.-F. Lohier, B. Norah, O. Delacroix, C. Alayrac, M. Taillefer and A.-C. Gaumont, *Chem. Eur. J.* **2013**, 19, 8760-8764.

[23] C. A. Bange and R. Waterman, *ACS Catal.* **2016**, 6, 6413-6416.

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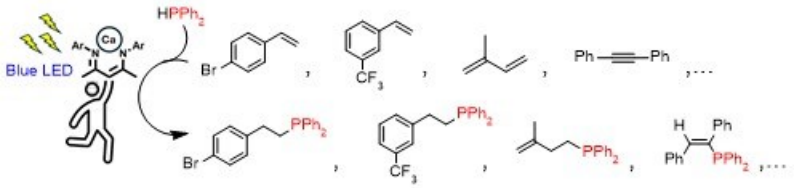

Calcium compounds are competent photocatalysts for hydrophosphination. Returning to the compounds reported by Barrett and Hill, visible light irradiation at ambient temperature activates simple calcium derivatives comparable to thermal catalysis. Ancillary ligands are key to radical versus non-radical reactivity under these conditions.

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