# Photocatalytic Hydrophosphination with Air-Stable and Commercially Available Bis(acetylacetonato)copper(II) ($Cu(acac)_2$)

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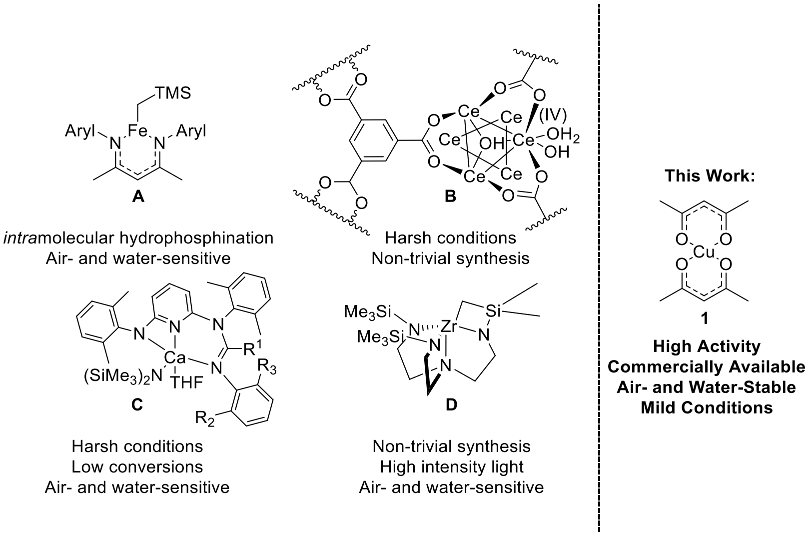
**ABSTRACT:** Bis(acetylacetonato)copper(II) ($Cu(acac)_2$, **1**), is active for the hydrophosphination of alkenes and alkynes with primary and secondary phosphines. Under thermal conditions, the activity of **1** is comparable to some of the best literature catalysts, but **1** is unique in that set possessing air- and water-stability. However, under ambient temperature irradiation centered at 360 nm, the conversions are remarkable with some reactions complete in minutes and several rarely reported unactivated substrates achieving high conversions within hours. The photocatalytic conditions are critical, and comparison to literature catalysts has been made in which **1** demonstrates superior activity. Initial mechanistic work does not suggest a radical mechanism rather the formation of a copper(I) active species. Hammett analysis indicates that depending on the substrate, either a nucleophilic or insertion-based mechanism may be at work. The enhanced reactivity provided by light also appears to be generalizable to other copper(I) compounds under irradiation, representing a broader phenomenon in metal catalyzed P–C bond formation. This simple, bench-stable, and inexpensive catalyst is highly effective, placing hydrophosphination in the hands of many more synthetic chemists.

## Introduction

Metal-catalyzed hydrophosphination is a potentially powerful tool in still-challenging P–C bond formation, despite the ubiquity of alkene substrates[1] and perfect atom economy of the transformation.[2] Phosphines are integral molecules in organic synthesis, catalysis, and are of importance in materials science and biologically active molecules.[3] However, hydrophosphination remains the domain of specialists. Many catalysts are air- and/or water-sensitive, are complicated to prepare, or suffer from limited substrate scope or modest activity.[4-7] Catalysts that are not readily available and easy to use do not augment the synthetic chemist's toolbox.[8]

A broadly applicable catalyst is one that also addresses some of the outstanding challenges of hydrophosphination. For example, unactivated alkene substrates remain underutilized, with limited success in a mere handful of examples.[9, 10, 11, 12, 13, 14] Webster reported an *intra*molecular hydrophosphination with an iron(II) β-diketiminato complex (Chart 1, compound A) with these substrates.[9] A cerium hydride metal-organic framework (Chart 1, compound B) is capable of intermolecular hydrophosphination with diphenylphosphine and unactivated alkenes upon extended reaction times at relatively high temperature (80 °C and 5 days).[10] Trifonov and coworkers identified calcium catalysts where the most active of them (Chart 1, compound C) capable of hydrophosphination of 1-nonene with phenylphosphine or diphenylphosphine in modest conversions.[11] Corma reported spare conversion of 1-octene to the hydrophosphination product when treated with diphenylphosphine and 10 mol % of $Cu(OTf)_2$·toluene over 24 hours at 100 °C.[12] We have identified that zirconium compounds (Chart 1, compound D) are capable for intermolecular hydrophosphination with unactivated alkenes, which initially suffered from sluggish reactivity.[15] In further investigations of this system, acceleration under photocatalytic conditions was observed, which was the critical feature for the high reactivity of triamidoamine-supported zirconium.[13] Though we started with primary phosphines as substrates,[13, 16] photocatalytic conditions availed a broader swath of substrates including secondary phosphines at reasonable reaction times at ambient temperature.[14] Substrate challenges dovetail into activity, and good progress has been made by Sarazin with barium[17] and ytterbium[18] catalysts at ambient conditions, but these are limited to styrene as substrate. Highly substituted alkenes still remain a challenge for catalytic hydrophosphination, though great progress has been made with stilbene by each Trifonov[19] and Cui.[20] It is easy to understand how these challenges would thwart better utilization of hydrophosphination in the synthetic community, despite the ubiquity of alkenes. The use of hydrophosphination in routine synthesis requires readily available, inexpensive catalysts that have established reactivity with a wide range of substrates.

**Chart 1: Examples of hydrophosphination catalysts that are active with unactivated alkenes**



Therefore, a search for a highly active, commercially available, air-stable, and base metal hydrophosphination catalyst was undertaken. Such a catalyst would allow hydrophosphination to become a more commonplace and synthetically usefully reaction for exploitation in late stage diversification of organic molecules. Beyond the preparation of P(III)–C bonds, simple oxidation of products would also afford P(V)–C bond as well, allowing for a greater range of bio-active products. The synthetic convenience of a single reaction to access both oxidation states of phosphorus is undeniable, and such a strategy leverages the order of magnitude lower cost of the secondary phosphine as precursor.[21]

Among base metals, iron is ideal. It has been the subject of on-going study in our hands [22, 23] and others' to good effect.[9, 24-28, 29] The criteria above, though, are yet to be fully met by iron, leading to an expanded search. Copper is a desirable metal due to its recyclability, relative abundance, low toxicity, and the air- and water-stability of many precursors that allow for easy handling.[30, 31] Based on literature studies, $Cu(acac)_2$ (**1**) was identified as an ideal candidate for our studies. Hydrophosphination of alkynes has been achieved by Oshima and coworkers with copper(I) iodide with cesium carbonate[32] and by Cui and coworkers using N-heterocyclic carbene (NHCs) ligands.[33] Hydrophosphination with a range of copper salts has been reported by Corma, which revealed that $Cu(OTf)_2$, $CuCl_2$, and CuCl, all catalyze the hydrophosphination of styrene derivatives with secondary phosphines at elevated temperatures and extended reaction times.[12] The Lipshutz group improved upon this copper catalysis by demonstrating hydrophosphination of α-substituted styrene derivatives and $Ph_2PH$ using $Cu(OAc)_2{\cdot}H_2O$ (**2**) in water and with the surfactant TPGS-750-M.[34] This study indicated that greater reactivity could be realized with copper. We hypothesized that photocatalysis may enhance reactivity to provide high reactivity and a broader substrate scope.

At the same time, copper bis(diketonato) compounds are effective in group 15 bond activation reactions with several examples of N–H activation in Ullman-type reactions and C–N coupling reactions.[35-39] Several groups have found **1** to be more effective at C–H amination reactions compared to other copper salts,[36, 37] and Beletskaya also demonstrated that **1** was an active catalyst for P–H bond activation and addition to alkynes with phosphorous(V) substrates.[40]

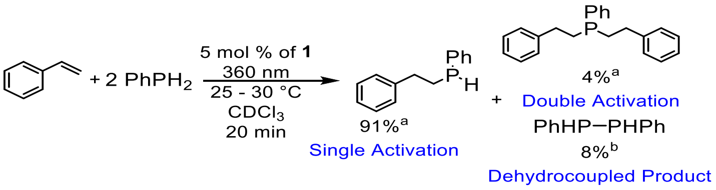
The sum of this analysis lead to the general hypothesis that highly successful hydrophosphination reactivity can be achieved by employing **1** as a pre-catalyst. This hypothesis has borne out, and herein is reported the substantial activity of **1** under 360 nm irradiation at ambient temperature. This overall high activity is accompanied by a significant substrate scope of alkenes and alkynes. For many substrates in this system, activity rivals or surpasses the activity of previous hydrophosphination reports with *any* metal and catalyst system. In this regard, **1** achieves the aim of an easy-to-use, highly active, and readily available hydrophosphination catalyst.

## Results and Discussion

### Optimization of Conditions

Hydrophosphination of styrene was examined first due to its common use in recent studies.[41, 42, 43, 44] A chloroform-$d_1$ solution of styrene was treated with 2 equiv. of phenylphosphine in the presence of 5 mol % of **1**. The mixture was irradiated with a broad wavelength 9-W UV/A lamp (see SI for details) at ambient temperature for 20 min, resulting in complete consumption of styrene as measured by $^1H$ NMR spectroscopy and 91% conversion to the anti-Markovnikov, single activation product $PhPHCH_2CH_2Ph$ as determined by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 1). Reactions with primary phosphines are often run with excess phosphine to minimize the double activation product, and indeed, small amounts of the tertiary phosphine with similarly limited amounts of 1,2-diphenyldiphosphine were observed. These byproducts and catalyst were readily separated by chromatography to afford product in 66% isolated yield. Isolation of phosphine products in these reactions is well described.[16, 34, 45]

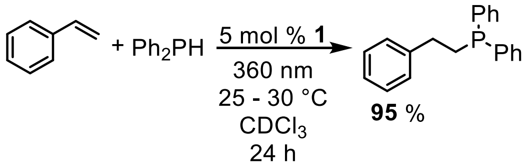
**Scheme 1**. Initial hydrophosphination of styrene with phenylphosphine by **1**.



[a] conversion of styrene determined by $^1$H NMR and $^{31}$P{$^1$H} NMR spectroscopy of three trials and integration to internal standard of 1,3,5,-trimethoxybenzene (See SI for note on determination of yields) [b] conversion of phosphine determined by $^{31}$P{$^1$H} NMR spectroscopy.

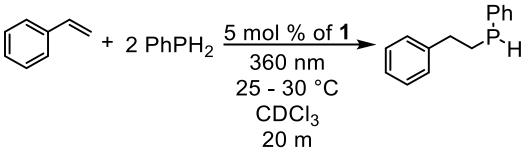
Initial screening demonstrated that secondary phosphines are also viable substrates. Treatment of styrene and 1 equiv., of diphenylphosphine with 5 mol % of **1** resulted in 85% conversion to $Ph_2PCH_2CH_2Ph$ as measured by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy after 5 h of 360 nm irradiation and 95% conversion was observed after 24 h of irradiation.

**Scheme 2**. Initial hydrophosphination of styrene with diphenylphosphine by **1**.



Several control reactions were then conducted in the reaction of 2 equiv. of phenylphosphine and styrene (Table 1). Under 360 nm irradiation in the absence of **1**, only 6% conversion was observed at 20 min, compared to 91% (vide supra). Reactions run in ambient light, at 60 °C with 5 mol % of **1**, went to 59% completion when measured at 20 min of heating, 79% after 45 min, and 90% after 75 min. For comparison, the temperature of the 360 nm photoreactor was measured to be 25–30 °C, depending on how long it had been in use. No efforts to control the temperature within this range were undertaken.

**Table 1.** Optimization of Conditions



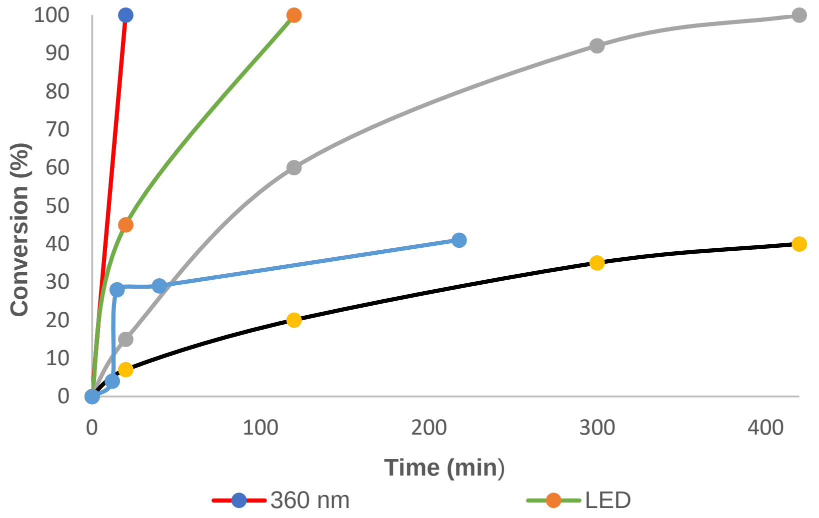
| Entry | Deviation from standard conditions | Conversion (%) |
|---|---|---|
| 1 | None | 100 |
| 2 | 1 eq $PhPH_2$ | 51 |
| 3 | Control; without **1** | 6 |
| 4 | Ambient light, 60 °C | 59 |
| 5 | Visible Light LED | 45 |
| 6 | Ambient light | 15 |
| 7 | Dark | 7 |
| 8 | 2 mol % of **1** | 100 |
| 9 | 1 mol % of **1** | 90 |
| 10 | 25 mol % of **1** | 40 |
| 11 | Neat | 100 |
| 12 | Benzene-$d_6$ solution | 100 |

Standard condition: 0.38 mmol (39.5 mg) of styrene and 0.76 mmol phenylphosphine (83.5 mg) and 0.19 mmol (5 mg) of **1** in 600 μL of $CDCl_3$. Changes in catalyst loading and phenylphosphine equivalents are with respect to styrene. Conversion to both secondary and tertiary phosphine determined by integration of $^1H$ and $^{31}P\{^1H\}$ NMR spectra.

Exploration of a wavelength dependence was undertaken with the phenylphosphine reaction at 5 mol % loading of **1** (Figure 1). Irradiation with visible light using a commercial LED bulb resulted in 100% conversion of styrene and 96% selectivity for the single activation hydrophosphination product $PhPHCH_2CH_2Ph$ in less than 2 h. Reactions under ambient light at ambient temperature proceeded to 15% completion in 20 min, 60% at 2 h, and 100% conversion of styrene with 96% selectivity for $PhPHCH_2CH_2Ph$ in less than 7 h. Reactions run in the dark resulted in only 7% conversion of styrene after 20 min, 42% after 18 h, and 58% after 44 h.

The photocatalytic nature of the reaction was established with an initiation experiment. A two-to-one mixture of phenylphosphine and styrene with 5 mol % of **1** was irradiated at 360 nm for a 3-minute interval and otherwise kept in the dark. After an initial 12 min with no irradiation, 4% conversion was measured by $^1H$ NMR spectroscopy. Then, following 3 min of irradiation, 28% conversion was measured. Subsequent monitoring of the reaction revealed nearly identical conversation after an additional 25 min in the dark, and the conversion only rose to 41% after 3 additional hours in the dark. The fast formation of product in the light that slows in the dark indicates that the reaction is photocatalytic rather than photoinitiated. Both behaviors have been observed for hydrophosphination catalysts.[13, 23, 46]

**Figure 1**. Light dependence of hydrophosphination of styrene with phenylphosphine by **1**.



Standard conditions: 0.38 mmol (39.5 mg) of styrene and 0.76 mmol phenylphosphine (83.5 mg) and 0.19 mmol (5 mg) of **1** in 600 μL of $CDCl_3$.

Several catalyst loadings were then tested for the hydrophosphination of styrene with two equivalents of phenylphosphine (Table 2). Complete consumption of styrene was achieved with 2 mol % of **1**. Decreasing the loading to 1 mol % of **1** resulted in 90% consumption of styrene and 79% NMR conversion of $PhPHCH_2CH_2Ph$. When the catalyst loading was increased to 25 mol %, 40% conversion of styrene was measured after 20 min of 360 nm irradiation. The non-linear dependence on catalyst is consistent with dimeric, oligomeric, or polymeric aggregation of catalyst, which is common for copper hydride and copper phosphide complexes.[47, 48] It also may be the result of a decreased relative concentration of phenylphosphine, an idea explored in further detail with additional mechanistic experiments.

Despite comparable activity with 2 mol % of catalyst, 360 nm irradiation with 5 mol % of **1** was used for ease of benchmarking with literature reports. It is recommended that new utilization of **1** should be initiated at 2 mol % and loadings increased if the substrates prove challenging. Similarly, reactions were run in chloroform-*d* as opposed to neat or in benzene-$d_6$ despite similar reactivity, due to ease of monitoring by $^1$H NMR spectroscopy.

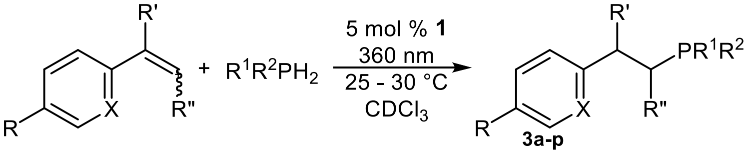
## Hydrophosphination of styrene derivatives

Treatment of para-substituted styrenes bearing electron withdrawing or donating substituents were amenable to these conditions and converted to the respective secondary phosphine product in >90% in 20 min when treated with 2 equiv. of phenylphosphine under 360 nm irradiation (Table 2, products **3a**-**e**). Similarly, 2-vinyl pyridine (Table 2 product **3f**) was amenable to these conditions. When these substrates were treated with 1 equiv. of diphenylphosphine, the tertiary phosphine products were formed in good to excellent yields in under 5 h with >90% conversion in less than 24 h (Table 2, products **3g-k**). Under these conditions, it was not empirically obvious that either electron donating or withdrawing substituents promote the reaction for either phenyl- or diphenylphosphine.

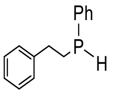
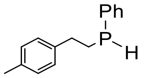
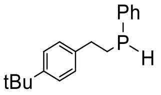
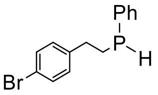
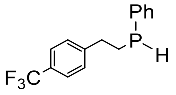
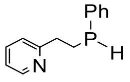
More sterically encumbered styrenes are accessible in this system as well. A cis/trans mixture of β-methylstyrene treated with phenylphosphine and **1** under irradiation resulted in 99% conversion in 20 h to previously unreported **3l**. The trans isomer does appear to go to completion faster, and it is unclear whether this is due to isomerization or steric factors. Treatment of α-methyl styrene and phenylphosphine with **1** under irradiation resulted in 92% conversion to **3m** in just over 2 h. When α-methyl styrene was treated with diphenylphosphine, 63% conversion to product **3n** was measured at 21 h. Increasing the amount of diphenylphosphine to 1.5 equiv. per alkene resulted in 83% conversion after 20 h of irradiation and indicates a possible dependence on phosphine concentration in the reaction. Additionally, 1.5 equiv. of diphenylphosphine was used in Lipshutz's study, which allowed for a comparison of copper catalysts and is discussed in a subsequent section.[34]

Phosphines with substituents other than phenyl, though not commonly reported,[4, 11, 49,] are viable in this system (Table 2, products **3o**-**3p**). Treatment of styrene with 2 equiv. of mesitylphosphine in the presence of 5 mol % of **1** gave quantitative conversion to product **3o** within 20 min, a more than 70 fold increase over previous reports.[11, 13] Reaction of 2 equiv. of cyclohexylphosphine with styrene and 5 mol % of **1** proceeded to 46% conversion to product **3p** after 28 h of 360 nm irradiation. The difference in reactivity suggests electronic factors play a role but steric factors confound that assessment.

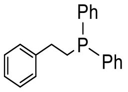
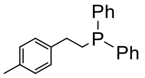
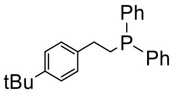
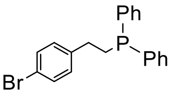
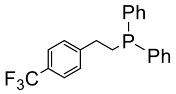
**TABLE 2. Hydrophosphination of styrene derivatives**



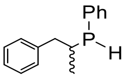
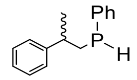
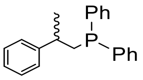
**Substrate Scope: phenylphosphine with styrene derivatives**[a]

| | | | | | |
|---|---|---|---|---|---|
|  |  |  |  |  |  |
| **3a** | **3b** | **3c** | **3d** | **3e** | **3f** |
| 100%[c] | 100%[c] | 100%[c] | 100%[c] | 100%[c] | 100%[c] |
| 91%[d, e, f] (66)[g] | 91%[d, e] | 94%[e] | 94%[e] | 96%[e] | 86%[e] |
| 20 m | 25 m | 20 m | 20 m | 20 m | 20 m |

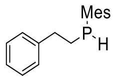
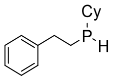
**Substrate Scope: diphenylphosphine with styrene derivatives**[b]

| | | | | |
|---|---|---|---|---|
|  |  |  |  |  |
| **3g** | **3h** | **3i** | **3j** | **3k** |
| 85%[e, f] | 98%[e] | 83%[d, e] | 88%[e] | 87%[e] |
| 5 h | 5 h | 5 h | 5 h | 5 h |

**Substrate scope: α/β substituted styrenes**

| | | |
|---|---|---|
|  |  |  |
| **3l** | **3m** | **3n** |
| 99%[a, e] | 92%[a, e] | 83%[b, e, h] |
| 20 h | 2h 15 m | 20 h |

**Substrate scope: primary phosphines**[a]

| | |
|---|---|
|  |  |
| **3o** | **3p** |
| 96%[e] | 46%[e] |
| 20 m | 28 h |

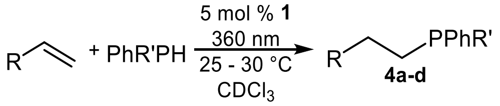
[a] 0.38 mmol unsaturated substrate and 0.76 mmol phenylphosphine [b] 0.38 mmol unsaturated substrate and 0.38 mmol diphenylphosphine [c] conversion of styrene starting material to secondary or tertiary hydrophosphination product by $^1$H NMR spectroscopy [d] conversion of hydrophosphination product as determined by comparison to internal standard of 1,3,5,- trimethoxybenzene or TMS [e] conversion determined by integration of $^1$H and $^{31}$P{$^1$H} NMR spectra for starting material to products (See SI for note on determination of yields) [f] average of three trials [g] isolated yield [h] 1.5 eq phosphine used (0.375 phosphine, 0.25 mmol unsaturated, 5 mol % of **1**)

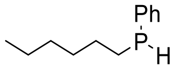
## Unactivated alkene substrates

Unactivated alkenes are a significant challenge and were explored next (Table 3). Treatment of terminal alkenes such as 1–hexene and 1–octene with 2 equiv. of phenylphosphine and 5 mol % of **1** gave greater than 70% conversion to the single activation, secondary phosphine product when monitored by $^{31}$P{$^1$H} and $^1$H NMR over 16 h or fewer under irradiation at 360 nm (products **4a** and **4b**). This is the fastest report of these substrates with primary phosphines to date.[11, 13] The only other report with a comparable yield is our previous report with zirconium under photolysis from a higher intensity 253.7 nm Hg arc lamp for 24 h.[13] Reaction with ethoxy ethene gave 81% conversation to product **4c** in 6 h, again the fastest and highest conversion observed to date.[13] Unactivated cyclic internal alkenes such as cyclohexene and ciscyclooctene were unreactive under these conditions. Reticence of such substrates has been observed in other copper-catalyzed reactions, which has been attributed to an increased barrier to insertion.[50]

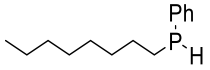
Secondary phosphines were more sluggish with these alkenes. Efficient conversion of these substrates has yet to be achieved without elevated temperatures and 3–5 days of reaction time.[10-12, 14] Treatment of 1-hexene with diphenylphosphine and 5 mol % of **1** under irradiation at 360 nm gave less than 20% conversion after 24 h. However, irradiation of a neat mixture of 1-hexene, and increasing to three equivalents of diphenylphosphine, and 5 mol % of **1** for 24 h resulted in 74% conversion to product **4d** as determined by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy. NMR spectra of this reaction mixture were broad, and crude separation from copper was performed for firm characterization of the tertiary phosphine product. Consistent with other studies, neat reactions can be more effective with **1**.[11, 22, 26]

**TABLE 3. Hydrophosphination of unactivated substrates with 1**

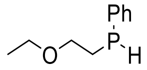




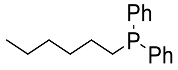
**4a**
72%[a]
7 h



**4b**
88%[a]
16 h



**4c**
82%[a]
6 h



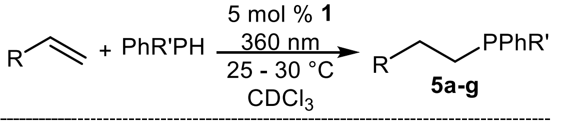
**4d**
74%[b]
24 h

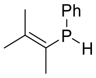
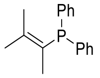
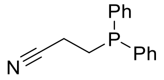
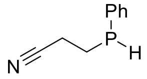
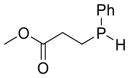
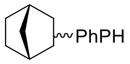
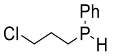
Conversions determined by integration of $^1$H and $^{31}$P{$^1$H} NMR spectra [a] 0.38 mmol unsaturated substrate and 0.76 mmol phosphine [b] neat with 0.38 mmol 1-hexene and 0.114 mmol $Ph_2PH$

## Other common hydrophosphination substrates

Several of the other frequently utilized unsaturated substrates were also tested (Table 4). Reaction of 2,3-dimethyl,1-3-butadiene afforded the 1,4-addition product within 80 min with phenylphosphine (product **5a**) and 8 h with diphenylphosphine (product **4b**) under photocatalytic conditions with 5 mol % of **1**. All Michael acceptors tested reacted rapidly with both phenyl- and diphenylphosphine (products **5c–e**). Initial NMR spectra obtained before irradiation indicated that full conversion methyl acrylate and acrylonitrile had occurred. While these activated alkenes are generally facile hydrophosphination substrates, uncatalyzed reactions are typically on the order of hours at elevated temperatures which was confirmed in control experiments without copper. Similarly, reactions at ambient temperatures with the best literature catalysts generally proceed over the course of an hour [51] or more.[29, 52] A strained internal alkene, norbornene, gave 99% conversion as determined by $^1$H NMR spectroscopy and 96% conversion as determined by $^{31}$P{$^1$H} NMR spectroscopy (**5f**). Although not a common hydrophosphination substrate, allyl chloride proceeds in 63% conversion to **5g** and further illustrates the functional group tolerance of this catalyst.

**Table 4. Hydrophosphination of other common hydrophosphination substrates**



| | | | |
|---|---|---|---|
|  |  |  |  |
| **5a** | **5b** | **5c** | **5d** |
| 99%[a] | 93%[b] | 90%[b, c,] | 98%[a, c] |
| 80 m | 8 h | 20 m | 25 m |
|  |  |  | |
| **5e** | **5f** | **5g** | |
| 99%[a] | 99%[a] | 63%[a, d] | |
| 10 m | 50 m | 18 h | |

Yields determined by integration of $^1$H and $^{31}$P{$^1$H} NMR spectra [a] 0.38 mmol of unsaturated substrate and 0.76 mmol of phenylphosphine [b] 0.38 mmol unsaturated substrate and 0.38 mmol diphenylphosphine [c] ambient light [d] yield determined by integration to internal standard of TMS

## Alkyne substrates

Treatment of internal and terminal alkynes under irradiation with either phenyl- or diphenylphosphine provided access to vinyl phosphine products (Table 5, entries 1-12). Reaction of 1-phenyl-1-butyne with 1 equiv. of phenylphosphine and 5 mol % of **1** under 360 nm irradiation for 24 h afforded the vinyl phosphine product in 81% conversion with 100% selectivity for P–C bond formation at the alkyl substituted position and a 3:1 preference for the Z-isomer (Table 5, entry 1). Reaction with 2 equiv. of phenylphosphine under the same conditions afforded the vinyl phosphine product in nearly quantitative conversion and 2.45:1 selectivity (Table 5, entry 2). Under both conditions, only trace amounts of the double hydrophosphination product were observed, [22, 33, 53-56] but this reaction was not pursued further.

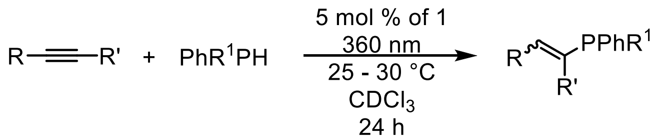
Symmetrical alkenes such as 3-hexyne and diphenylacetylene, proceed in poor yield with one equivalent of phenylphosphine and moderate yields with two equivalents of phenylphosphine under irradiation with 5 mol % of **1** (Table 5, entries 3-6). The stereoselectivity for these reactions were opposite, where 3-hexyne gave slight selectivity for the *E*-isomer while diphenylphosphine moderately favored the *Z*-isomer.

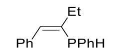
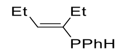
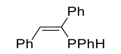
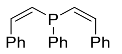
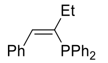
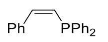
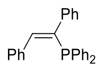
Different reactivity was observed when terminal alkynes such as phenylacetylene were treated with 2 equiv. of phenylphosphine, which resulted in activation of both P–H bonds to form tertiary divinyl phosphines with a 3:1 selectivity for the *Z,Z* isomer over the *E,Z* isomer (Table 5, entry 7). Reducing the amount of starting phosphine to 0.5 equivalents affords 92% conversion in 20 h with nearly identical selectivity for the *Z,Z* isomer (Table 5, entry 8).

Reaction of a 1:1 mixture of diphenylphosphine and phenyl-1-butyne with 5 mol % of **1** under 360 nm irradiation for 24 h resulted in 74% conversion with 100% selectivity for P–C bond formation at the alkyl substituted position and a 4.8:1 preference for the *E*-isomer (Table 5, entry 9). However, the *Z:E* selectivity appears to be variable as a replication of this reaction under identical conditions resulted in 75% conversion but 1:1.1 selectivity. This behavior has been observed before and could be attributable to UV[4] or on metal isomerization.[57] Yields can be improved by using excess phosphine as demonstrated with phenylacetylene which goes to 41% completion when treated with 1 equiv. of diphenylphosphine and 77% completion when treated with 2 equiv. (Table 5, entry 10 and 11).

Diphenylacetylene proceeded poorly with 1 equiv. of phenylphosphine reaching 12% conversion after 24 h (Table 5, entry 12). When the above reaction was run with 5 mol % of $PPh_3$, a trivial difference was observed over 24 h (Table 5, entry 13). Added $PPh_3$ has improved copper catalysis in other systems.[58, 59] Modest improvements could also be made by running the reaction neat (Table 5, entry 14) or by adding a second equivalent of diphenylphosphine with a longer reaction time. Reactions run with 2 equiv. of diphenylphosphine reached 19% conversion after 20 h and 36% conversion after 72 h (Table 5, entry 14).

**TABLE 5. Hydrophosphination of alkynes**



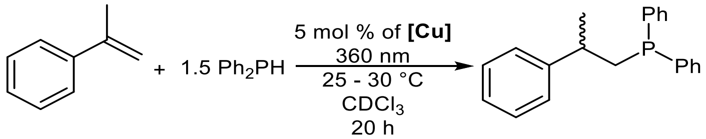
| entry | R | R' | RR'PH | Major Product[a] | Conversion %[b] | *Z:E* |
|---|---|---|---|---|---|---|
| 1 | Ph | Et | $PhPH_2$ |  | 80 | 3:1 |
| 2 | Ph | Et | 2 $PhPH_2$ |  | 99 | 2.45:1 |
| 3 | Et | Et | $PhPH_2$ |  | 48 | 1:1.7 |
| 4 | Et | Et | 2 $PhPH_2$ |  | 71 | 1:1.5 |
| 5 | Ph | Ph | $PhPH_2$ |  | 40 | 1.9:1 |
| 6 | Ph | Ph | 2 $PhPH_2$ |  | 58 | 2.1:1 |
| 7 | Ph | H | 2 $PhPH_2$ |  | 86[c, d] | 3:1[e] |
| 8 | Ph | H | 0.5 $PhPH_2$ |  | 88[c, f] | 2.7:1[e] |
| 9 | Ph | Et | $Ph_2PH$ |  | 74 | 4.8:1 |
| 10 | Ph | H | $Ph_2PH$ |  | 41 | 32:1 |
| 11 | Ph | H | 2 $Ph_2PH$ |  | 77 | 37.5:1 |
| 12 | Ph | Ph | $Ph_2PH$ |  | 12 | 1:0 |
| 13[g] | Ph | Ph | $Ph_2PH$ |  | 11 | 10:1 |
| 14 | Ph | Ph | 2 $Ph_2PH$ |  | 19[d](36[h]) | 35:1[h] |

Conditions: 0.38 mmol of alkyne and 0.38 or 0.76 mmol of $PhPH_2$ or $Ph_2PH$ and 0.019 mmol **1** [a] only the major stereoisomer is depicted [b] conversion to anti-markovnikov vinyl phosphine as determined by integration of $^1H$ and $^{31}P\{^1H\}$ NMR spectra [c] double P-H bond activation product [d] 20 h [e] ratio of *Z,Z:E,Z* product [f] 1 h [g] 5 mol % of $PPh_3$ added [h] 72 h

## Benchmarking to the literature

Benchmarking is an important endeavor in catalysis,[60] and among reports of copper-catalyzed hydrophosphination,[12, 32-34, 61] Lipshutz's copper(II) acetate monohydrate, $Cu(OAc)\cdot{}_2H_2O$ (**2**), stands out as highly active.[34] That study focused on **2** in the catalytic hydrophosphination of styrene and α-substituted styrene derivatives with $Ph_2PH$ in water utilizing the surfactant, TPGS-750-M. While water is a potentially attractive solvent, added surfactants are not, and to draw broader conclusions to the field, comparison reactions were run in $CDCl_3$. A model of the literature reaction utilizing 5 mol % of **2**, the same concentration of α-methyl styrene (0.25 mmol) and $Ph_2PH$ (0.375 mmol), and stirring under ambient light and temperatures, but substituting $CDCl_3$ for a water/ TPGS-750-M mixture resulted in less than 25% conversion of α-methyl styrene with diphenylphosphine in 20 h (Table 6, entry 1). This contrasts with 95% conversion over the same time frame in water/ TPGS-750-M reported by Lipshutz (Table 6, entry 2). However, irradiation of a $CDCl_3$ solution containing α-methyl styrene, 1.5 equivalents of diphenylphosphine, and 5 mol % of **2** in a J-Young type NMR tube resulted in a 76% conversion in 20 h (Table 6, entry 4). Irradiating a $CDCl_3$ solution of 5 mol % of **1**, α-methyl styrene, and 1.5 equivalents of diphenylphosphine under the same conditions resulted in 83% conversion after 20 h (Table 6, entry 5). Thus, for laboratories without access to TPGS-750-M, irradiating under 360 nm light in organic solvent or neat solution of **1** or **2** is a convenient alternative.

**Table 6. Benchmarking to the literature**

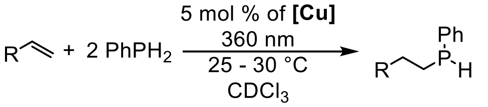


| Entry | Catalyst | Conditions (light; solvent; stirring) | Conversion %[a] |
|---|---|---|---|
| 1 | **2** | Ambient light; $CDCl_3$; stirring | 25 |
| 2 | **2** | Ambient light; Water/TPG-750-M; stirring | 95[b] |
| 3 | **2** | Ambient light; $CDCl_3$ | 6[c] |
| 4 | **2** | 360 nm; $CDCl_3$ | 76 |
| 5 | **1** | 360 nm; $CDCl_3$ | 83 |

Conditions: 0.25 mmol of alkene and 0.375 mmol of phenylphosphine 0.0125 mmol catalyst [a] conversion determined by integration of $^1H$ and $^{31}P\{^1H\}$ NMR spectra. [b] reported by Lipshutz.[34] [c] 17 h

We also sought to benchmark under our conditions (Table 8). Interestingly, with primary phosphines, the activity of **2** appears to be slightly less active than **1**, which is the opposite trend to what was observed with secondary phosphines. Treatment of styrene with 2 equiv. of phenylphosphine with 5 mol % of **2** under what was otherwise our model photocatalytic conditions resulted in 86% conversion after 20 min (Table 8, entry 1), slightly less than the 100% conversion observed with **1** (Table 8, entry 2). Treatment of 1-hexene with 2 equiv. of phenylphosphine with 5 mol % of **2** under what was otherwise our model photocatalytic conditions resulted in 68% conversion after 24 h (Table 8, entry 3) vs 80% conversion with 5 mol % **1** over the same time period (Table 8, entry 4).

**Table 7. Comparison of 1 and 2 with primary phosphines**



| Entry | catalyst | Time | Alkene | Phosphine | Conversion %[a] |
|---|---|---|---|---|---|
| 1 | **2** | 20 m | styrene | $PhPH_2$ | 86 |
| 2 | **1** | 20 m | styrene | $PhPH_2$ | 100 |
| 3 | **2** | 20 h | 1-hexene | $PhPH_2$ | 68 |
| 4 | **1** | 20 h | 1-hexene | $PhPH_2$ | 80 |

Conditions: 0.38 mmol of alkene and 0.76 mmol of phenylphosphine 0.019 mmol catalyst [a] conversion determined by integration $^1H$ and $^{31}P\{^1H\}$ NMR spectra. For styrene this includes conversion to both secondary and tertiary phosphines.

## Mechanistic insights

Several lines of inquiry including, observation of modeled catalytic reactions, a comparison of copper precursors, isotope labeling experiments, stoichiometric model reactions, and a Hammett analysis in the context of the literature understanding of related copper catalysis provide a working mechanistic hypothesis.

In some examples, **1** is a precursor to copper oxide nanoparticles in the presence of organic molecules under thermal conditions.[62, 63] Several observations argue against this pathway. Previous reports of nanoparticle formation result in the formation of acetic acid and acetone byproducts that are not detected in this system.[62] As a test of homogeneity of the active catalyst, 450 mg of elemental mercury (Hg) was added to the reaction of $Ph_2PH$ and styrene catalyzed by 5 mol % of **1** to sequester any precipitated copper.[64] Observed reactivity was identical to reactions conducted without added Hg, suggesting that Cu(0) is not precipitating and is consistent with visual observation of a homogenous system. While these data are not definitive, they are consistent with molecular catalysis.

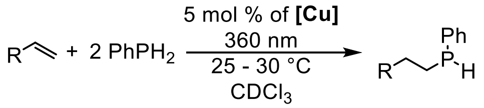
Radical reactivity is another possibility with redox active copper. As an initial test for radical reactivity, a reaction with two equivalents of phenylphosphine with styrene and 5 mol % of **1** was conducted in the presence of 10 mol % of

2,2,6,6- tetramethylpiperidine-N-oxyl (TEMPO)[64] under photocatalytic conditions. Observed reactivity was identical to the reaction conducted without TEMPO. The lack of inhibition from TEMPO is inconsistent with a radical based process. Additional study of this possibility is underway.

## Comparison of bis(β-diketonato) precursors

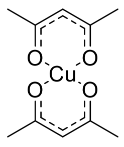
To test the role of the β-diketonate ligand in the reaction, copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate) (**6**) and copper bis(2,2,6,6-tetrafluoro-3,5-heptanedionate) (**7**) were synthesized and their reactivity explored (Table 6). When styrene was treated with 2 equiv. of phenylphosphine and 5 mol % of **1** or **6** under photocatalytic conditions almost identical reactivity was observed and both catalysts gave quantitative conversion (Table 6, entry 1 and 2). Diminished reactivity was observed when this reaction was catalyzed with 5 mol % of **7**, with only 30% conversion of styrene (Table 6, entry 3) converted over the same reaction time. The same trend was observed in reactions with 1-hexene as greater than 70% conversion was observed with both compound **1** (Table 6, entry 4) and **6** (Table 6, entry 5) compared to 44% conversion with compound **7** (Table 6, entry 6). Additionally, $^1H$ NMR signals attributed to acetylacetone or 2,2,6,6-tetramethyl-3,5-heptanedione were detected in reaction mixtures with **1** or **6**. However, the corresponding β-diketone 1,1,1,5,5,5-hexafluoroacetylacetone was not observed in NMR spectra of reaction mixtures with **7**. Thus, it is likely that the decreased reactivity of **7** is a result of slower protonation of the less basic β-diketonate.

**Table 8. Comparison of copper(II) bis(β-diketonato) precursors**

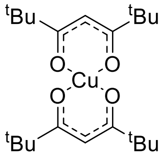


| Entry | Catalyst | Time | alkene | Conversion %[a] |
|---|---|---|---|---|
| 1 | **1** | 20 m | styrene | 100 |
| 2 | **6** | 20 m | styrene | 100 |
| 3 | **7** | 20 m | styrene | 30 |
| 4 | **1** | 20 h | 1-hexene | 80 |
| 5 | **6** | 24 h | 1-hexene | 72 |
| 6 | **7** | 24 h | 1-hexene | 44 |
| 7 | None | 24 h | 1-hexene | 4 |

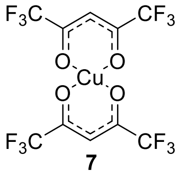
Conditions: 0.38 mmol of alkene and 0.76 mmol of phenylphosphine 0.019 mmol catalyst [a] conversion to both secondary and tertiary phosphine determined by integration of $^1H$ and $^{31}P\{^1H\}$ NMR spectra.



**1**



**6**



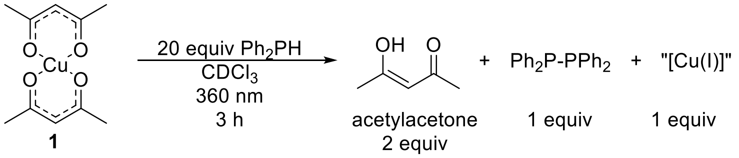
**7**

## Catalyst activation

To better understand the activation of **1**, a systematic analysis of several parameters in the reaction was performed. Treatment of 5 mol % of **1** with styrene resulted in no observable reactivity as determined by $^1H$ NMR spectroscopy. In contrast, treatment of 5 mol % of **1** with $Ph_2PH$ resulted in the formation of acetylacetone and tetraphenyldiphosphine ($Ph_2P–PPh_2$, Scheme 2) indicating that P–H bond activation and formal protonation of **1** with release of acetylacetone are the initial steps in generating the catalytically active species. Importantly, quantitative activation of **1** is not immediate. An initial $^1H$ and $^{31}P\{^1H\}$ NMR spectrum of this reaction mixture demonstrated liberation of 0.45 equiv. of acetylacetone in a 1.55:1 ratio with $Ph_2P–PPh_2$. This behavior indicates that several copper species that are potentially catalytically active may be generated. Irradiation of this sample over 3 h resulted in the continued increase in concentration of both products until 2 equiv. of acetylacetone were detected and 10% conversion of $Ph_2PH$ to $Ph_2P-PPh_2$ had occurred. Continued irradiation of the sample beyond 3 h resulted in no change in the concentration of acetylacetone and only a small increase in the conversion of $Ph_2PH$ to $Ph_2P-PPh_2$. When measured at 4 h, 15% conversion to $Ph_2P–PPh_2$ had occurred and the signal for the P–H bond of $Ph_2PH$ had broadened significantly in the $^1H$ NMR spectrum. At 20 h, 15% of $Ph_2PH$ had been consumed with an 11% conversion to $Ph_2P–PPh_2$ along with and several decomposition products (See SI for a graph and further details). Glueck and coworker have previously observed that unidentified phosphine oxides are common in reactions of Cu(I) with phosphines,[65] and similar byproducts are present in some hydrophosphination reactions with **1**. Repetition of this reaction with less solvent indicated that the complete activation of **1** is faster at higher concentrations of reactants and may account for the observed concentration dependence of catalysis (vide supra). Additionally, control reactions run in the dark demonstrate that both the formation of acetylacetone and $Ph_2P–PPh_2$ proceeded faster under irradiation and may suggest one of the roles of light in this system. Furthermore, the correlation between the formation of acetylacetone and $Ph_2P–PPh_2$ in these experiments suggest they are related processes.

The formation of $Ph_2P–PPh_2$ could be through reductive elimination from a Cu(II) phosphido intermediate species as has been observed with other metals,[2] a single electron transfer (SET) from $Ph_2P^-$ to reduce **1** and subsequent coupling of two •$PPh_2$ radicals, or a bimetallic process. Regardless of pathway, literature and experimental observations point to generation of a Cu(I) species,[9, 11, 30, 31, 35, 58, 59, 65, 66, 67, 68] and reactions in the absence of unsaturated substrate implicate a copper phosphido intermediate in that process.

**Scheme 2:** Reaction of **1** with 20 equiv. of diphenylphosphine

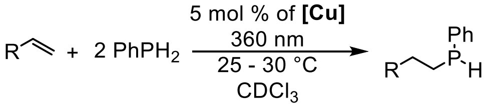


In Corma's study with $Cu(OTf)_2$, a copper(I) active catalyst was proposed based on the observed loss of an EPR signal upon treating $Cu(OTf)_2$ with $Ph_2PH$ among other results.[12] Single electron transfer (SET) reductions of copper(II) compounds by electron rich substrates are well established,[30, 31] and precedent for the reduction of copper(II) β-diketones in the absence of a reducing agent comes from Tabacchi and others.[66, 67] Müller observed the in situ reduction of Cu(II) to Cu(I) in heterogeneous hydroamination reactions, and several groups have reported copper(I) hydride catalyzed hydrosilylation[59, 69] and hydroamination[58] with **2** and a phosphine ligand upon the addition of a silane reductant.

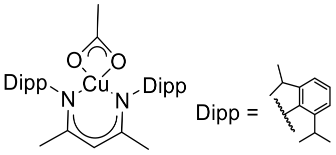
## Reactivity of Cu(I) vs. Cu(II) precursors

Tetrakis(acetonitrile)copper(I) hexafluorophosphate ($[Cu(CH_3CN)_4]PF_6$, **8**)[70] copper(I) oxide ($Cu_2O$, **9**), triphenylphosphine copper(I) hydride hexamer ($[(PPh_3)CuH]_6$, **10**), and a β-diketiminato copper(II) compound (**11**) were screened for differences in reactivity based on the formal oxidation state of copper. All catalysts tested were successful at catalyzing the hydrophosphination of styrene and phenylphosphine, at varying relative rates, under the same photocatalytic conditions (Table 7, entries 1–3). However, the same pattern was not observed for catalyzing 1-hexene and phenylphosphine. Copper(I) compounds **8, 9,** and **10** were active with 1-hexene to various degrees (Table 7, entries 4–7) while **11** was inert to hydrophosphination of 1-hexene (Table 7, entry 8). This suggests copper(I) is more suited to that substrate and further points to an in-situ reduction of **1** (vide infra). Though not an ideal comparison due to the bulky 2,6-diisopropylphenyl substituents of **11**, the stronger chelation of the β-diketiminate of **11** compared to the more basic diketonate of **1** may prevent the reduction and account for the dramatic difference in reactivity between the two compounds.

**Table 9. Comparison of copper(I) and (II) precursors**



| Entry | catalyst | Time | Alkene | Phosphine | Conversion % |
|---|---|---|---|---|---|
| 1 | $Cu(CH_3CN)_4PF_6$ (**8**) | 20 m | styrene | $PhPH_2$ | 45 |
| 2 | $Cu_2O$ (**9**) | 20 m | styrene | $PhPH_2$ | 15 |
| 3 | $[(PPh_3)CuH]_6$ (**10**) | 20 m | styrene | $PhPH_2$ | 68 |
| 4 | **11** | 20 m | styrene | $PhPH_2$ | 41 |
| 5 | **8** | 16 h | 1-hexene | $PhPH_2$ | 26 |
| 6 | **9** | 24 h | 1-hexene | $PhPH_2$ | 73 |
| 7 | **10** | 24 h | 1-hexene | $PhPH_2$ | 70 |
| 8 | **11** | 24 h | 1-hexene | $PhPH_2$ | 1 |
| 9 | **10** | 5 h | styrene | $Ph_2PH$[b] | 78 |



**11**

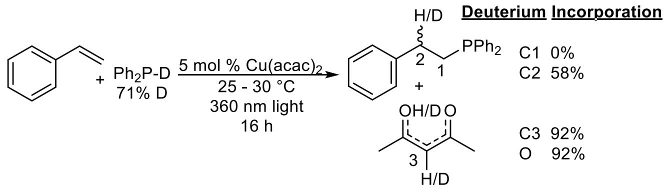
Conditions: 0.38 mmol of alkene and 0.76 mmol of phenylphosphine 0.019 mmol catalyst [a] conversion determined by integration of $^1H$ and $^{31}P\{^1H\}$ NMR spectra. [b] 1 eq

Copper(II) phosphido compounds are rare,[71] and there are a limited number of copper(I) phosphido compounds known.[33, 48, 72-76] [77] Potentially related copper(I) phosphido compounds are $(PPh_3)CuPPh_2$ and $[(Ph_2PH)CuPPh_2]_n$ reported by Caulton and coworkers.[48] We were unable to prepare pure samples of $(PPh_3)CuPPh_2$ as reported for comparison. However, the similar reactivity between **1** and **10** is intriguing and was considered a proxy given that one route to $(PPh_3)CuPPh_2$ is reaction of **9** with $Ph_2PH$. Furthermore, the observation that $PPh_3$ did not negatively impact catalysis with **1** when added to reaction mixtures in several replicated reactions with both alkenes and alkynes is consistent with a Cu(I) phosphido intermediate. Though not isolated, $[(Ph_2PH)CuPPh_2]_n$ was reported from the addition of multiple equivalents of $Ph_2PH$ to $Cu(O^tBu)_4$. Compound **1** when treated with one, two, four, eight and 20 equivalents of $Ph_2PH$ provided data consistent with observations made of $[(Ph_2PH)CuPPh_2]_n$. A yellow solution was formed in these reactions with $J_{PH}$ = 311 Hz, which compares favorably to the literature report. A similar trend was observed for the $Ph_2PH$ signal in the $^{31}P\{^1H\}$ NMR spectra. The signal was shifted downfield when one equivalent of diphenylphosphine was added and the signal shifted back upfield toward the value of free diphenylphosphine as more $Ph_2PH$ was added to solution, as was seen in the literature. Attempts at crystalizing a discreet intermediate from these solutions resulted only in powders that were insoluble in common organic solvents, which was the purpose of adding $PPh_3$ in the original study. Therefore, it is likely that akin to Caulton's report, an oligomeric or polymeric copper(I) phosphido can be formed under catalytic conditions.

## Deuterium labeling experiments

Deuterium labeling studies were undertaken to address the mechanism of P–C bond formation. Styrene was treated with one equivalent of $Ph_2PD$ (71% deuterium) and 5 mol % of **1** under irradiation and monitored by $^1H$, $^2H$, and $^{31}P\{^1H\}$ NMR spectroscopy. Signals attributable to 58% deuterium incorporation at C2 (Scheme 4) of the hydrophosphination product as well as those at the oxygen and C3 of acetylacetone were observed (Scheme 4). Exchange was not detectable at any other positions of products. Multiple deuterium exchanges at acetylacetone indicate that there is more complex chemistry associated with this ligand. Importantly, it explains the lack of complete incorporation on the hydrophosphination product. The potential steps that would yield the isotopomers observed include a 2,1 insertion of styrene into a copper phosphido intermediate or a 1,2 insertion of alkene into a copper hydride intermediate. There is insufficient data to distinguish these possibilities.

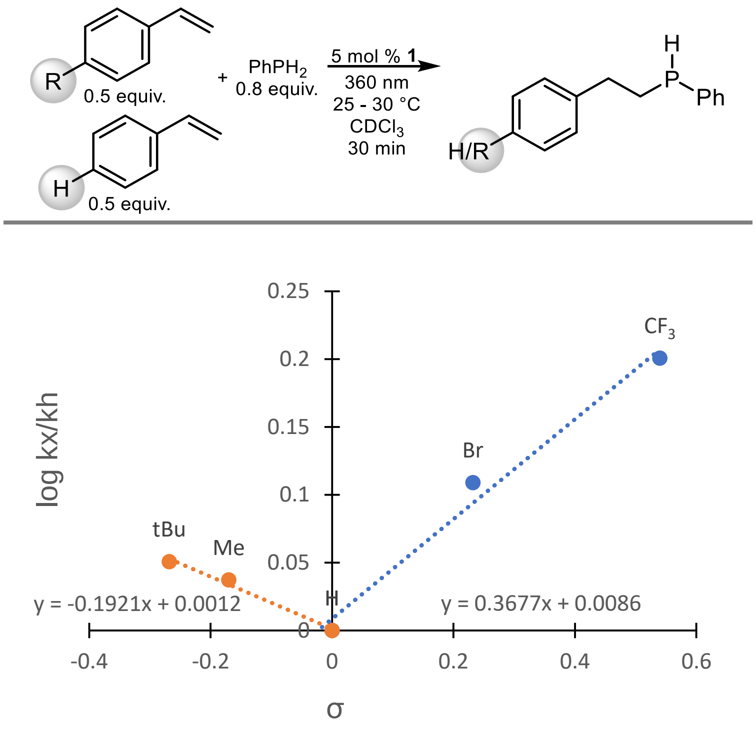
**Scheme 4. Deuterium incorporation of hydrophosphination product and acetylacetone**



A Hammett analysis[78] via competition experiment was performed to better understand electronic effects of the phosphine. Equimolar amounts of $Ph_2PH$ (0.5 eq) and $(4\text{-}MeOPh)_2PH$ (0.5 eq) or $(4\text{-}MePh)_2PH$ (0.5 eq) were treated with 0.8 equiv. styrene as the limiting reagent with 5 mol % of **1** under irradiation. The more electron rich and acidic $(4\text{-}MeOPh)_2PH$ underwent faster conversion and generated more of the hydrophosphination product. This indicates that acidity and/or nucleophilicity of the phosphine is important in catalysis.

A second Hammett analysis was performed to better understand electronic effects of the substrates in the reaction, which were not apparent from relative apparent rates (Scheme 5). In this experiment, the functional group on the para-positions of the unsaturated substrates were varied. A concave plot was observed. This behavior commonly indicates a change in mechanism upon introduction of different substituents,[79] which helps explain the high activity of **1** towards both electron rich and poor unsaturated substrates. The high activity of **1** towards electron-poor substrates is consistent with nucleophilic attack of a copper phosphido on an unsaturated substrate, and is indeed the mechanism of most late metal hydrophosphination catalysts.[2] However, the high activity of **1** towards unactivated substrates is inconsistent with a nucleophilic mechanism and argues for an insertion mechanism. Cui has previously proposed insertion of terminal alkynes into the Cu–P bond of NHC-copper phosphido compounds.[32] The Hammett data for our system may indicate that a nucleophilic mechanism is dominant with alkenes with electron withdrawing substituents and an insertion-based mechanism is predominant with electron donating substituents on styrene and with unactivated substrates.

**Figure 2. Hammett study of para-substituted styrene derivatives and $PhPH_2$ with 1**



These data are informative but do not address the role of light in the reaction. For zirconium, evidence of a P n → Zr d ligand-metal charge transfer that resulted in lengthening of the Zr–P bond made substrate insertion more favorable was found.[13] It is suspected that a charge transfer event is also responsible for the enhanced activity of **1** under photolysis, though promotion may be directly into a σ* orbital. The absence of a well-identified intermediate in this study make further analysis by computation too speculative for useful results. Nevertheless, this catalysis is clearly photocatalytic, and the yellow color of these reactions is indicative of an absorption that trails into the UV, which explains the effective 360 nm irradiation. However, without a discrete copper species isolated or identified, spectroscopic study of the absorption bands is complicated, and these conclusions are tenuous. Continued study of this phenomena is warranted and underway. For these reasons, and the uncertainties differentiating between 2,1 and 1,2 insertion presented above, a catalytic cycle would be too speculative to include in this report. However, these studies support redox activation of copper, formation of a copper-phosphido intermediate, and differential P–C bond formation based on substrate, all of which are features that inform further catalyst development.

## Concluding Remarks

Commercially available Cu(acac)$_2$ (**1**) has been demonstrated to be a rapid and efficient hydrophosphination pre-catalyst for a diverse collection of phosphines and unsaturated substrates at ambient temperature under low intensity UV-A irradiation. This is the first report of an air- and water-stable compound capable of the catalytic hydrophosphination of unactivated substrates. Compound **1** is active with both primary and secondary phosphines, but significantly more so with the former, an underrepresented class of substrates.[4] Both alkenes and alkynes are functionalized in this system, with **1** demonstrating greater activity with alkenes. Evidence points to a Cu(I) active species and either an insertion-based or nucleophilic pathway, depending on the nature of the unsaturated substrate.[4] The success of irradiation of now copper and previously zirconium compounds supports photocatalysis as a general method for achieving highly active hydrophosphination catalysis. Additionally, this work further demonstrates that continued study of common laboratory reagents under new conditions, can yield new and exciting reactivity.[80] Continued study of this system for mechanistic insight expansion of copper-catalyzed hydrophosphination is underway.

## Experimental Section

### General information

All manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glovebox or standard Schlenk techniques unless otherwise noted. $CDCl_3$ was purchased and then degassed and dried over calcium hydride and then distilled and stored over 3 and 4 Å molecular sieves. Diphenylphosphine was synthesized according to literature procedures and stored under an inert atmosphere of $N_2$ prior to use.[81] Compounds **6**,[82] **7**,[83] **8**,[84] **10**[85] **11**[86] and $Ph_2PD$[87] were synthesized according to literature procedures. All other reagents were acquired from commercial sources and dried by conventional means, as necessary. ESI-mass spectra were collected on an AB-Sciex 4000 QTrap Hybrid Triple Quadrupole/Linear Ion trap mass spectrometer. $^1H$, $^2H$, $^{13}C$, $^{31}P$, $^{31}P\{^1H\}$ and $^{31}P$ HMBC NMR spectra were recorded at 25 °C with a Bruker AXR 500 MHz or Varian 500 MHz spectrometer.

**Safety note**: Phosphines are toxic, and many primary phosphines are volatile. Redox reactions or metal catalysts have the potential for rapid hydrogen evolution from phosphine substrates. Appropriate precautions for toxic gases and hydrogen are necessary in this work.

## General procedure for catalytic experiments

In an $N_2$ filled dry box, 0.76 mmol of phosphine (or 0.38 mmol where applicable) and 0.38 mmol of unsaturated substrate (and internal or external standard where applicable) were measured and mixed in 0.6 mL $CDCl_3$. This solution was either pipetted into a shell vial containing 0.019 mmol of catalyst in 100 µL of $CDCL_3$ or catalyst was added via stock solution. The resulting 6 mL solution was quickly transferred to either an aluminum foil wrapped J-Young type polytetrafluoroethylene-valved NMR tube or an NMR tube with a disposable NMR cap, which was subsequently wrapped with parafilm. For reactions containing an external standard, a sealed capillary containing 5 mg of $PPh_3$ was added to the NMR tube before capping. Upon removal from dry box, the outside of the tube was washed with a 50:50 water: bleach to remove trace amounts of malodorous phosphine on the outside of the tube. An initial $^1H$ and $^{31}P\{^1H\}$ NMR spectra was then obtained as soon as possible. After the initial NMR spectra, reactions were removed from the aluminum foil and placed in a photoreactor containing a Rexim G23 UV-A (9W) lamp (unless otherwise noted) at ambient temperature and shielded from external light. Periodic $^1H$ and $^{31}P\{^1H\}$ NMR spectra were collected. Conversions were determined by integration of $^1H$ and $^{31}P\{^1H\}$ NMR spectra to starting materials and in many cases (see note in SI) confirmed by internal standard of either 1,3,5-trimethoxy benzene,[25] tetramethyl silane, or an external standard of $PPh_3$.

## Associated Content

## Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

- Experimental procedures, spectroscopic data, supplementary figures and tables, and photographs and description of the photocatalysis reactor

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## Notes

The authors declare no conflict of interest.

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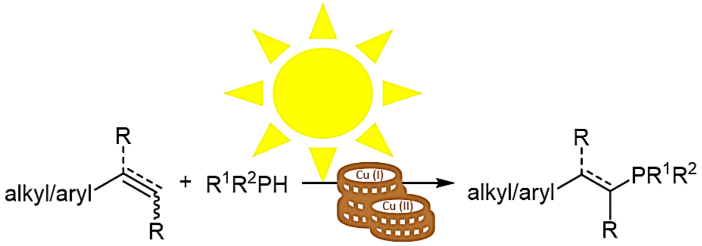
# Table of Contents artwork



difficult substrates

commercially available pre-catalyst

short reaction times