A rare study into the catalytic hydrophosphination of allenes is reported. Employing an Fe(II) β-diketiminate pre-catalyst, the reaction of HPPh$_2$ proceeds with a range of aryl- and alkylallenes. For arylallenes, the E-vinyl product forms as the major species, while the 1,1-disubstituted alkene is formed in a larger ratio than the Z-vinyl product (e.g., 6:3:1 as E/1,1/Z). The use of H$_2$PPh results in good yields of the 1,1-disubstituted alkene, where the resultant secondary phosphine product does not undergo further reaction. We postulate a catalytic cycle based on spectroscopic data. Employing an [Fe(salen)]$_2$-μ-oxo pre-catalyst leads to phosphine dehydrocoupling rather than hydrophosphination.

**Key words** iron, homogeneous catalysis, hydrophosphination, allenes, phosphines

Allenes are emerging as a key building block in organic synthesis owing to their unique reactivity, variety of functionalization modes and relative ease of synthesis. Of particular interest in recent years have been routes to forming carbon–heteroatom bonds using allenes as organic substrates. There has been a great deal of interest in the catalytic hydroamination of allenyl substrates, as well as hydroboration and hydrosilylation methods. These reactions generate complex and multi-functional compounds in a straightforward and atom-efficient manner.

Compared to these elements however, there are relatively few studies involving phosphorus-based functionalization of allenes (Scheme 1). This is somewhat surprising given how often the hydrophosphination of styrenes, aryl acetylenes and even heterocumulenes is reported in the literature. These reactions potentially offer new and unusual organophosphorus compounds, as well an atom economical reaction pathway to them. Various routes to and classes of allenylphosphonates have been reported, and these have been shown to be capable of undergoing further intramolecular and intermolecular reactions. Enantioselective hydrophosphinylation has also been reported. In terms of hydrophosphination chemistry, Mitchell initially reported the addition of diphenylphosphine over allenes through radical addition. More recently, rare-earth- and transition-metal-catalyzed methods have been developed. Takagi reported an ytterbium-catalyzed route followed by oxidative workup leading to phosphate oxide products, while Busacca reported using phosphine-boranes as a P(III) source requiring a stoichiometric equivalent of a metal hydride. In addition, Leung has demonstrated a double hydrophosphination reaction with applications in ligand design. There are also a range of palladium-catalyzed reactions using P(V) sources of phosphorus, including hydrophosphination using pinacol phosphonate, hypophosphorous acid and H-phosphonates. Lu and co-workers have used a catalytic amount of
a tertiary phosphine to undertake [3+2] cycloadditions of allene substrates, forming cyclopentene products. More recently, this transformation was studied in detail by Ofial and co-workers, with vinyl phosphonium intermediates being trapped to allow characterization of the phosphine addition products, the chemoselectivity of which is similar to that obtained from a hydrophosphination reaction.

We have previously reported hydrophosphination reactions utilizing alkenes and alkynes catalyzed by various iron complexes, as well as nickel-catalyzed and base-mediated methods. We were interested to see if iron complexes, as well as nickel-catalyzed and base-mediated methods, could be employed as precatalysts. Care must be taken when operating under these conditions to avoid dehydrocoupling. However, there are conflicting reports in the literature. For example, Westerhausen et al. have reported that hydrophosphination of allenes can be achieved with iron complexes, but the reaction is regioselective towards the internal bond over the internal bond (51% vs 23% conversion).

Initial reaction optimization studies were undertaken using phenyllallene (PA) and diphenylphosphine (HPPH2) as reagents. Based on the wealth of previous studies where 1 is employed as a pre-catalyst, care must be taken when optimizing the hydrophosphination reaction in order to minimize competing phosphine dehydrocoupling (forming P2Ph4 and H2) and allene polymerization reactions. Our initial set of reaction conditions employed 5 mol% of 1, a 1:1 ratio of PA/HPPH2 and generated the terminal E isomer 3B as the major hydrophosphination product, but the major reaction product was P2Ph4 (Scheme 2).

Performing the reaction at room temperature with 1 led to very low conversion, and at raised temperatures with equimolar amounts of reagents the chemoselectivity towards hydrophosphination is still poor, although it is improved with stirring (see Scheme 2). A drop-off in conversion is observed without stirring, along with a large amount of Ph2P being produced. Surprisingly, a slight excess of HPPH2 (0.1 mmol excess relative to PA) shows a drop-off in overall conversion, but this is predominantly due to the dehydrocoupling pathway being switched off. A further increase in HPPH2 loading (to 1 mmol in total) shows a modest increase in conversion, where more of the unusual 1,1-disubstituted (herein referred to as ‘internal’) hydrophosphination product 3C forms. Even with this excess, no doubly-hydrophosphinated products are observed. A change in solvent to CD2Cl2 does not alter the hydrophosphination product distribution. In contrast, using a slight excess of PA (0.6 mmol PA:0.5 mmol HPPH2) leads to high chemoselectivity towards the hydrophosphinated products (51% 3B, 23% 3C, 8% 3A).

We observed three distinct products that can be distinguished through both 31P and 1H NMR (see the Supporting Information for full characterization of products). The reaction is reasonably regioselective towards functionalization of the terminal bond over the internal bond (51% vs 23% conversion), and strongly stereoselective towards the E isomer over the Z isomer (51% vs 8% conversion). The strong E selectivity is in-line with the generally E- or non-selective catalytic outcomes when preparing these compounds from 1-methyl-1-propyne. It is worth commenting on the conflicting reports of the formation of the E or Z isomer (3B or 3A) reported in the literature from the reaction of HPPH2 and 1-methyl-1-propyne: Mitchell and Heesche reported (E)-diphenyl(1-phenylprop-1-en-2-yl)phosphane (i.e., 3B) appearing at +6.8 ppm in the 31P NMR spectrum and (Z)-diphenyl(1-phenylprop-1-en-2-yl)phosphane (i.e., 3A) appearing at −14.8 ppm in the 31P NMR spectrum. This review is based on the literature, whereby 3A is stated to appear at a negative ppm value (approximately −14 ppm) and 3B is stated to appear at a positive ppm value (approximately +7 ppm).

We would expect that a phosphorus atom located trans across a dou-
ble bond to a phenyl group might experience greater deshielding than a phosphorus atom located trans across a double bond to a proton; coupled with the evidence provided by Westerhausen, we favor 3A appearing at −13.3 ppm and 3B appearing at +8.4 ppm in CDCl₃. On top of this, although complex, 3A, 3B and 3C display clear coupling in the ³¹P NMR spectra such that we can assign the signals with reasonable confidence (Figure 1). It is important to note that when mixtures of products form, the 2-dimensional correlation of ¹H and ³¹P NMR spectral data, and thus assignment of the products, is not trivial.

Although [Fe(salen)]₂⁺μ-oxo complex 2 is a highly active pre-catalyst for the hydrophosphination of styrenes and acrylates, it does not perform well in this hydrophosphination reaction. Using 2 instead of 1 under these conditions does not result in the same high chemoselectivity, highlighting the importance of the catalyst structure in reaction control. It is surprising that 2 is a highly competent pre-catalyst for dehydrocoupling HPPh₂.

We further sought to apply this reactivity to other allene substrates (Figure 2). A range of functionalized arylallenes are tolerated in similar conversions and selectivity to PA. Electron-rich substrates give particularly high hydrophosphination conversions, ranging from 74% to 91%; total hydrophosphination conversions of 74% for o-OMe-PA and 91% for o-OMe-PA are observed, which is surprising given the steric hindrance present in these two starting materials and their products. There is a decrease in hydrophosphination conversion for strongly electron-withdrawing p-F-PA, but this is observed as 4% (11A), 54% (11B) and 1% (11C), so although the overall conversion is modest, the selectivity for 11B is excellent. For all arylallenes there is a preference for the formation of the terminal E isomer over the terminal Z and internal isomers, although the specific ratio of the three products does vary. In general, there is a larger quantity of the unusual internal isomer C formed when electron-rich PA substrates are employed (compare electron-poor substrates p-Cl-PA 9 and p-F-PA 11 to methyl and methoxy substrates 4–8). Using cyclohexylallene (Cy-A, 12) generates five isomeric products (see the Supporting Information) rather than three, although the overall conversion is low at 40%. Hydrophosphination of methoxyallene (OMe-A, 13) yields only the two terminal products, as well as a small amounts of the double hydrophosphination product, but again the conversion is relatively poor.

Several alternative phosphorus reagents were also tested in catalysis with PA. HPCy₂ is considerably less active than HPPh₂ (Table 1, entry 1). Excitingly, reactions with H₂PPh form the internal product 15C with good selectivity and a good overall yield (entry 2). No double hydrophosphination is observed, even when H₂PPh is used in excess (entry 3). In contrast, H₂PCy does not hydrophosphinate at all under these reaction conditions. In all cases the corresponding P–P-bonded product is not observed. This is likely due to the higher reaction temperature needed (110 to 120 °C) to undertake dehydrocoupling of HPCy₂, H₂PPh or H₂PCy with pre-catalyst 1.²⁶

![Figure 1](image-url)  
**Figure 1** Key coupling interactions observed for 3A, 3B and 3C via ³¹P and ¹H NMR spectroscopy

![Scheme 2](image-url)  
**Scheme 2** Optimization of the reaction (deviation from initial conditions listed). Conversions determined by inverse-gated ³¹P NMR spectroscopy with PP₃ as an internal standard and reported relative to HPPh₂ consumption unless noted. * Conversion relative to allene using ¹H NMR with 1,3,5-trimethoxybenzene as an internal standard. † 1 mol% of 2 used and CH₃CN employed instead of C₆D₆.
We have previously conducted mechanistic investigations into the hydrophosphination of alkynes using $1$ and HPPh$_2$, and the reaction reported herein appears to have similarities. We can rule out nanoparticle involvement through poisoning experiments, while radical-clock reactions appear to confirm the hydrophosphination reaction is not radical-mediated, but the competing dehydrocoupling reaction is likely to be a radical process. The reaction is unaffected by the presence of benzaldehyde, which appears to rule out a nucleophilic phosphorus-based mechanism where we might expect to see reaction with the carbonyl if an intermediate of the form $[$Fe$]$–PPh$_2$ acts as a nucleophile toward the allene, and thus an anionic center is present during the catalytic cycle. When using DPPh$_2$ in the hydrophosphination of PA we observe regioselectively mono-deuterated products, which are formed in a similar ratio as the reaction with HPPh$_2$ (Scheme 3). This indicates that the hydrophosphination step is direct rather than proceeding through product or substrate rearrangement, or reversible protonolysis steps.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate (H$<em>n$PPh$</em>{3-n}$)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>1</td>
<td>HPC$_2$ (14)</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>H$_2$PPh (15)</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>H$_2$PCy (16)</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>H$_2$PCy (16)</td>
<td>0</td>
</tr>
</tbody>
</table>

*a* Conditions: 0.6 mmol PA, 0.5 mmol phosphine, 0.025 mmol 1, 0.6 mL C$_6$D$_6$. Conversions determined by inverse-gated $^3$P NMR spectroscopy with PPh$_3$ as an internal standard and reported relative to HPPh$_2$.

*b* 1.0 mmol H$_2$PPh used; conversion relative to PA.
We propose the initial activation of 1 involves the formation of an iron-phosphido complex by reacting with HPPH₂, releasing Si(Me)₄, which is observed in the in situ ¹H NMR spectra (Scheme 4). Similar compounds have been previously prepared, although stoichiometric reactions of 1 and HPPH₂ lead to only Ph₄P₂ being isolated, which highlights the reactive nature of the iron-phosphido species. The iron-phosphido intermediate can then add across one of the unsaturated carbon–carbon bonds; the regio- and stereoselectivity are determined by the bond added over (and for the terminal products, the face added across). The iron–carbon bond can then be cleaved by protonolysis with a second molecule of HPPH₂, generating the hydrophosphinated product. Although the resulting product is unsaturated, it is less amenable to further reactivity, largely due to steric effects, preventing double hydrophosphination. We propose that the regiochemistry observed, although clearly driven towards the thermodynamic E-product B, may have other factors at play. For example, with sterically hindered o-Me-PA only 8% of 6C is formed, compared to 27% of 4C (from p-Me-PA), so it can be argued in this case that steric limitations influence the formation of the C product, favoring the B product (60% of 6B vs 48% of 4B). In contrast, this trend is not enacted when we compare p-OMe-PA to o-OMe-PA, the same conversion to 7B and 8B is observed (60%), but this time a greater conversion to 8C is observed (21% of 8C compared to 11% of 7C); clearly a simple steric argument does not hold true here. However, there may be transient coordination of the o-OMe group in the iron-allyl intermediate that benefits 8C. However, we have not been able to crystallize, or observe by NMR spectroscopy, any long-lived intermediates.

To further prove the likelihood of a catalytic event that forms an on-cycle iron-phosphido intermediate, we employed less sterically encumbered β-diketiminate species 1’ in a stoichiometric reaction with HPPH₂. Orange crystals of complex 1’·PH₂ were isolated following reaction at 60 °C for 1 hour and crystallization at ~20 °C (Figure 3). Heating 1’·PH₂ in an attempt to release SiMe₄ from the complex only leads to decomposition.

To test the hypothesis that the production of internal product C is, in some cases, limited by steric influence from the β-diketiminate ligand, the less sterically demanding pre-catalyst 1’ was employed. Taking PA, p-Me-PA, p-OMe-PA and p-Cl-PA as test substrates, we observed an increase in selectivity for 3C, 4C, 7C and 9C (Table 2).
Agilent machines as stated. ¹H, ¹³C and ²H chemical shifts were referenced to residual solvent peaks, while ³¹P and ³¹P{¹H} NMR were referenced to PPh₃ (5.3 ppm). Mass spectrometry data was obtained using an Agilent 6545 Q-ToF LC/MS spectrometer. FTIR data was collected on a PerkinElmer Spectrum 100 FT-IR Spectrometer. All manipulations were carried out under an inert atmosphere using standard Schlenk/glove box techniques unless stated.

### Crystallographic Data for 1c-PPh₃ (Using Cu-Kα Radiation)

All experiments were conducted at 150 K, solved using SHELXS and refined using SHELXL via the Olex2 interface. Crystallographic data for 1c-PPh₃ have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2178990 (1c-PPh₃) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

### Hydrophosphination; General Procedure

Experiments were performed under an argon atmosphere in an M-Braun glove box. To a flame-dried J-Young ampoule of approximately 20 mL volume was added the required pre-catalyst (0.025 mmol, 5 mol%). To this was added the required allene (0.6 mmol) and phosphine (0.5 mmol). The ampoule was then sealed and heated, with stirring, for the times and conditions reported.

Spectroscopic conversions were determined by decanting the reaction mixture into a J-Young NMR tube at the end of the reaction and calculating the conversion by inverse-gated ³¹P NMR using PPh₃ as an internal standard. The solvent was then removed from the reaction, and the hydrophosphination products were isolated through column chromatography (silica gel, 80% petroleum ether/20% DCM as the eluent) under air. For the majority of products this work-up yields the phosphine products, although a small amount of phosphine oxides are observed in ³¹P and ¹H NMR. Some reactions generated products that oxidize rapidly in air – these were isolated from the catalyst by means of filtration through a silica plug under an argon atmosphere using 100% pentane as the eluent. These are noted in the product characterization section.

See the Supporting Information for analysis data and spectra.

### Conflict of Interest

The authors declare no conflict of interest.

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### Supporting Information

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References


