Article

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Regioselective Single and Double Hydrophosphination and Hydrophosphinylation of Unactivated Alkynes

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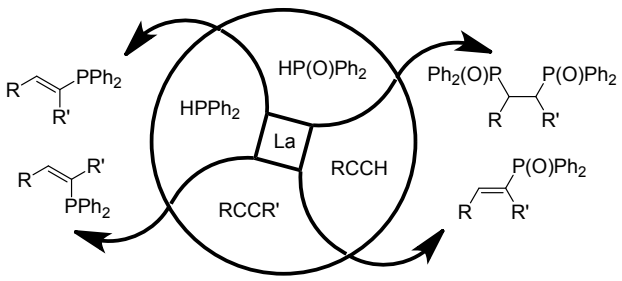
Abstract

A lanthanum-based *N,N*-dimethylbenzylamine complex was used as a precatalyst for both hydrophosphination and hydrophosphinylation of alkynes under mild conditions. In the case of hydrophosphination, the catalyst induced mono-addition with high regiospecificity, yielding only the anti-Markovnikov product, and stereoselectivity that could be controlled based on the reaction conditions. Undertaking the catalysis with excess phosphine yielded the *E* isomer as the major product; however, using excess alkyne, the *Z* isomer was instead isolated as the major product. A brief investigation into the catalytic cycle suggested that a dimeric form of the lanthanum phosphide active catalyst provided the *Z* isomers as kinetic products that then underwent isomerization to yield the final *E* isomers. In the case of hydrophosphinylation, the chemoselectivity depended on the nature of the alkyne used. Terminal alkynes gave only double addition products while both single and double addition products were successfully isolated in the case of internal alkynes. The hydrophosphinylation also showed high chemo- and regioselectivity as only the anti-Markovnikov products were isolated. Mono-hydrophosphinylation of internal alkynes gave almost exclusively the *E* isomer and double hydrophosphinylation of all alkynes led to 1,2-addition products.

Keywords: Hydrophosphination, Hydrophosphinylation, Lanthanum, Vinylphosphine, *E*-alkene, *Z*-alkene

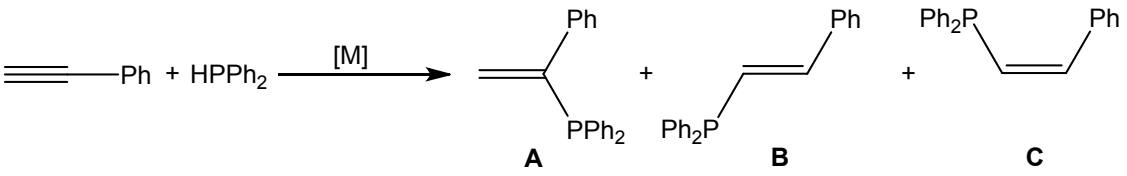
TOC Graphic:



Introduction

Phosphines and phosphine oxides are among the most common ligands utilized in the field of organometallic chemistry.[1] Nearly every type of catalytic reaction takes advantage of phosphine ligands in one fashion or another. Phosphines are attractive ligands because of their broad steric and electronic tunability.[2] Traditional phosphine synthesis has employed radical, super basic, or acidic conditions; however, these reactions commonly lack chemo-, regio- and stereoselectivity.[3] In an effort to improve selectivity, the catalytic addition of H-P and H-P(O) across unsaturated systems, referred to as hydrophosphination and hydrophosphinylation, respectively, has been investigated in recent years.[4] Traditionally, palladium, platinum, and some early transition metals have been used in catalytic hydrophosphination and hydrophosphinylation, and although these reactions show high chemoselectivity, they often still lack regio- and stereoselectivity (Table 1).[3b, 5] Additionally, with the use of various designer ligands, some earth abundant metals such as iron, copper, calcium, and the lanthanides have been successful in the hydrophosphination and hydrophosphinylation of unsaturated systems.[6, 7]

Table 1. Selected Examples of Previously Published Simple Metal Catalysts and Their Corresponding Selectivity



Catalyst [M]	Conditions	Yield (%) (**A:B:C**)
$Pd(PPh_3)_4$	CH_3CN, 130 ^oC, 18h	95 (0:14:86)
$Pd(OAc)_2$	CH_3CN, 130 ^oC, 7h	89 (87:7:6)
$Pd(PPh_3)_4$ + AcOH	CH_3CN, 180 ^oC, 12h	>92 (92:4:4)
$Ni[P(OEt)_3]_4$	C_6H_6, 80 ^oC, 10h	>93 (10:45:45)
$NiBr_2$	C_6H_6, 80 ^oC, 10h	85 (86:14:0)
$Ni(acac)_2$ + $HP(O)(OEt)_2$	C_6H_6, 80 ^oC, 10h	90 (95:5:0)
$Co(PMe_3)_4$	Toluene, 80 ^oC, 2h	73 (0:0:100)
Cp*FeMe(CO)py	Toluene, 110 ^oC, 48h	90 (0:10:90)
$(IMe_4)_2Yb(N(SiMe_3)_2)_2$	C_6H_6, 25 ^oC, 1h	>95 (0:15:85)

Many catalyst systems utilize bidentate phosphine ligands, where two phosphorus atoms coordinate to the same metal center, represented most famously by dppe ligands and their derivatives.[1] One method to produce a bidentate phosphine ligand is through the double hydrophosphination/hydrophosphinylation of alkynes. Hydrophosphination has been achieved with solvent-free radical conditions, but has required high temperatures and long reaction times.[8] Catalytic double addition reactions have also been successful using both early and late transition metal catalysts.[9] Recently, Nakazawa *et al*. described iron catalysts for the double hydrophosphination of terminal aryl alkynes. Unfortunately, the reaction required three days of

heating at 110 °C.[6a] Webster *et al.* also used an iron (II) catalyst for the intramolecular hydrophosphination of alkenes and alkynes, once again requiring elevated temperatures and lengthy reaction times.[6e] Recently, Waterman *et al.* used a dimeric iron complex to induce the double hydrophosphination of alkynes, requiring light or heat.[10] Copper catalysts have been used in the double hydrophosphination of both aryl and aliphatic alkynes. Though the copper systems required low catalytic loading, they too required high temperatures.[11] In related chemistry, europium has been successful in the single hydrophosphination of alkynes, although the reaction was not stereospecific and again required high temperatures.[12]

Similar to the double hydrophosphination reactions outlined above, double hydrophosphinylation of alkynes has also been investigated broadly. Han *et al.* successfully double hydrophosphinylated terminal alkynes using a strong base (LiO^{t}Bu) and high temperatures.[3e] Rhodium catalysts were also used to hydrophosphinylate alkynes under microwave irradiation and yielded mono- or double addition products depending on the loading of the phosphine oxide.[13] Manganese and rhenium catalysts have also been used to effect the single or double hydrophosphinylation of terminal aryl acetylenes although both required high temperatures.[14]

Overall, the hydrophosphination and hydrophosphinylation of acetylenes are both known reactions that have been achieved using a variety of catalysts. In the reported systems, these addition reactions have thus far only been studied independently and have not been examined simultaneously utilizing the same catalytic system. Both reactions generally required high temperatures and elongated reaction times with limited selectivity. Herein, we describe the first lanthanum-based catalyst, to our knowledge, capable of both hydrophosphination and

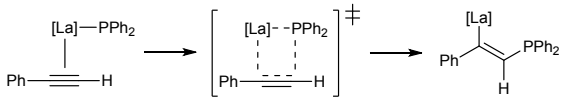
hydrophosphinylation of acetylenes under very mild conditions (25-60 °C) with tunable chemo- and stereoselectivity.

Results and Discussion

Recently, we reported the catalytic effectiveness of an α-metalated dimethylbenzylamine lanthanum complex ($La(Dmba)_3$) in the double hydrophosphinylation of unactivated nitriles under mild conditions; the reaction showed regioselectivity based on the nature of the nitrile.[15] In an attempt to further expand the utility of these lanthanum catalysts in hydrophosphination and hydrophosphinylation reactions, unactivated alkynes were investigated as alternative substrates.

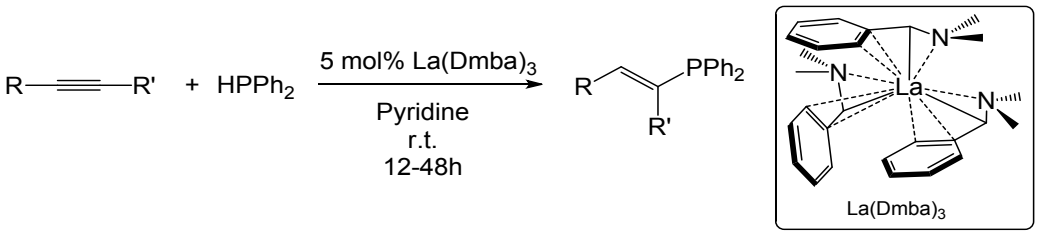
$La(Dmba)_3$ proved to be an effective precatalyst for the hydrophosphination of alkynes with diphenylphosphine. The reactions reached completion in 12-48 h with 5 mol% catalytic loading in pyridine at room temperature while using a 1:1.6 alkyne to diphenylphosphine ratio. Pyridine was selected as the solvent because we previously showed that it solvated both hydrophosphination and hydrophosphinylation active catalysts.[15] The reactions proceeded to 100% conversion when using aryl alkynes, giving exclusively the anti-Markovnikov product in all cases (Table 2). The catalysts showed tolerance to both electron donating and even slightly acidic alkynes (Table 2, **2d**), and the reaction was successful when using both internal and terminal aryl alkynes. In contrast, aliphatic alkynes, both terminal (1-hexyne) and internal (4-octyne), yielded no hydrophosphination even at high temperatures and elongated reaction times. Only a highly activated internal aliphatic alkyne was successfully hydrophosphinated (Table 2, **2g**). Double addition products were not observed when reacting with excess diphenylphosphine, even with heating and longer reaction times, while the *E* alkene monoaddition isomer was the major product in all cases. In an effort to explore the catalytic cycle, the hydrophosphination of

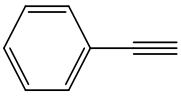
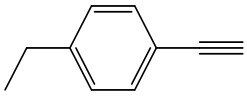
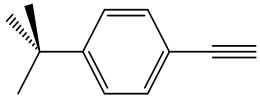
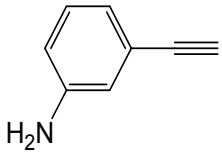
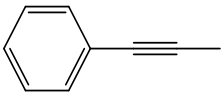
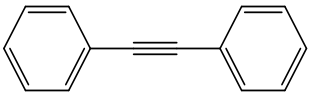
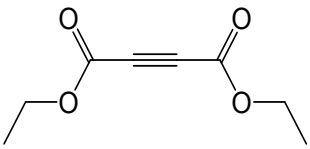
phenylacetylene (Table 2, **2a**) was monitored hourly via $^{31}P\{^{1}H\}$ NMR spectroscopy in d_5-pyridine. To our surprise, initially only the *Z* isomer ($^{31}P\{^{1}H\}$ = -23.5 ppm) was observed, which then proceeded to slowly isomerize to the *E* isomer ($^{31}P\{^{1}H\}$ = -10.0 ppm). This observation seems counterintuitive to the expected [2+2] addition mechanism, which would be predicted to form the *E* product directly (Scheme 1). Because of the unexpected stereochemistry found in the kinetic product, we began to wonder if the process was more complicated than merely a simple insertion reaction at a single metal center. In order to make sure that catalyst decomposition was not playing a role in the process, a hydrophosphination reaction between phenylacetylene and diphenylphosphine was set up with the usual conditions and allowed to react for 12 hours. An aliquot removed from the solution showed no evidence of leftover diphenylphosphine and a 95:5 ratio of *E*:*Z* alkenes. Addition of another portion of reactants (phenylacetylene and diphenylphosphine) led to continued catalytic reaction with complete conversion to product after another 12 hours and retention of the expected 95:5 isomer ratio.



Scheme 1. Typical [2+2] addition mechanism, portrayed with anti-Markovnikov addition of a lanthanum phosphide to phenylacetylene. Note that subsequent protonation of the La-C bond would give the *E* isomer (*trans* alkene).

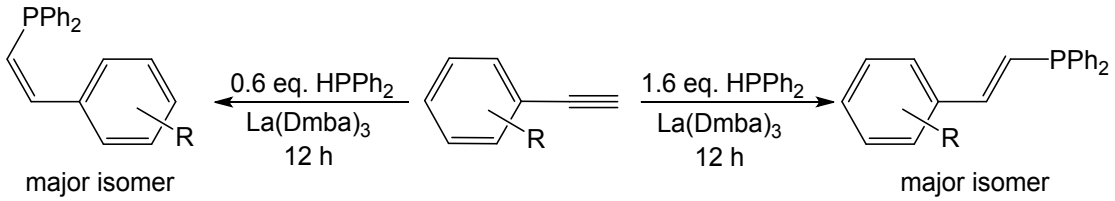
Table 2. Hydrophosphination of Internal and Terminal Alkynes



Entry	Alkyne (R on left; R' on right)	Reaction Time (h)	Yield (%)[a]	E:Z[b]
2a		12	87	95:5
2b		12	82	95:5
2c		12	85	95:5
2d		12	73	90:10
2e		12	90	80:20
2f		48	65	80:20
2g		48	60	95:5

Catalytic reactions were carried out with $La(Dmba)_3$ (13.5 mg; 5 mol%), acetylene (0.5 mmol) and diphenylphosphine (0.8 mmol) in pyridine (2 ml) for 12-48 h at room temperature. [a] Isolated yields. [b] Ratio determined by $^{31}P\{^1H\}$ NMR spectroscopy.

Furthermore, when the reaction was carried out under the same conditions, but with reversed ratios of 1:1.6 diphenylphosphine to alkyne, the *Z* isomer became the major isomer produced with only small amounts of the *E* isomer formed after 12 hours. This proved to be the case with all three different alkynes tested in this way (Scheme 2). Further control experiments showed that the isomerization did not occur with heating, elongated reaction time, light, Lewis acid catalyst, or diphenylphosphine catalyst, nor without lanthanum tris-phosphide active catalyst. This further supports the idea that the *Z* isomer is the kinetic product of the hydrophosphination, which then undergoes isomerization catalyzed by lanthanum phosphide to produce the thermodynamic *E* isomer. Thus, not only was the hydrophosphination regiospecific, but its stereoselectivity could be controlled depending on the reactant ratios used for the reaction.



R= H	88%	**(2a')**	(>95% *Z*)	R= H	87%	**(2a)**	(>95% *E*)
4-Et	85%	**(2b')**	(>95% *Z*)	4-Et	82%	**(2b)**	(>95% *E*)
3-NH_2	80%	**(2d')**	(>80% *Z*)	3-NH_2	73%	**(2d)**	(>90% *E*)

Scheme 2. Stereoselectivity depends on diphenylphosphine loading

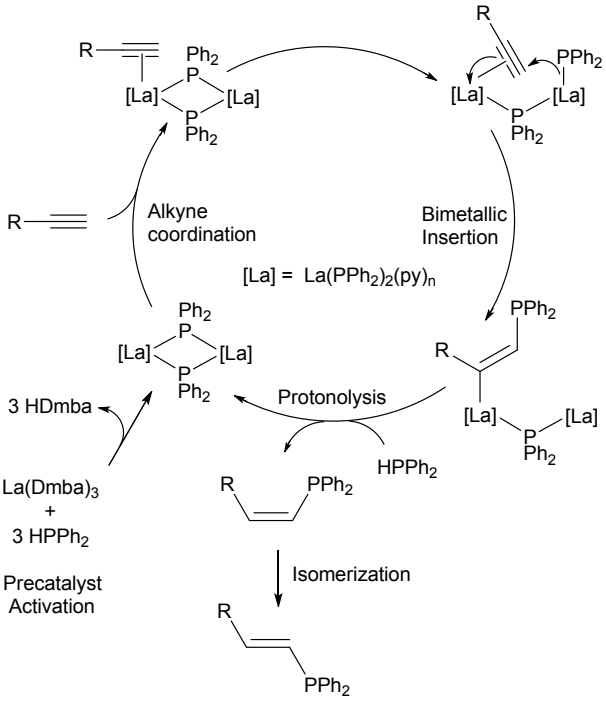
Based on the stereochemical observations made above, it became clear that the reaction mechanism does not follow the traditional monometallic insertion ([2+2] addition) followed by protonolysis mechanism (Scheme 1). To understand the catalytic cycle further, some additional

experiments were carried out. Using an internal standard, the stoichiometric reaction of $La(Dmba)_3$ with diphenylphosphine was shown to yield three equivalents of neutral dimethylbenzylamine (HDmba), while concurrently forming only the lanthanum tris-phosphide complex as the active catalyst. To investigate catalyst order, the hydrophosphination of phenylacetylene was monitored via ^1H NMR spectroscopy in d_5-pyridine every two minutes using three different catalyst loadings (2.5, 3.5, and 5.0 mol%; see Supporting Information). Since the isomerization requires the active lanthanum tris-phosphide complex, a slight excess of alkyne was used to suppress the isomerization, forming almost only the *Z* alkene. This data suggests that the catalysis is second order in lanthanum.

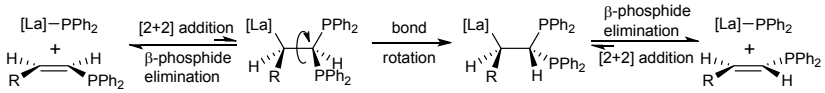
In the hydrophosphination of alkynes, mechanisms involving catalysts using first-row transition metals are among those investigated in the greatest detail, although previous reports have led to more questions than answers unfortunately.[6e, 11, 16] For example, experimental results in the case of iron catalysis have shown that the initial hydrophosphination occurred with primarily the *Z* configuration that gradually transformed to the *E* isomer, much like we have observed herein.[6a] A subsequently reported extensive DFT study on this iron-based system failed to effectively elucidate the reasons behind the observed selectivity.[16] In fact, the final mechanistic scheme presented in that report shows a standard [2+2] addition mechanism (giving the *E* isomer kinetically, despite the contrast between this and the experimentally observed results).[16] The *Z* isomer's presence is explained by an undefined isomerization reaction between *E* and *Z* isomers while bound to the metal center.[16] Another study involving NHC coordinated copper catalysts determined a slight energetic preference for the *E* product (only 0.7 kcal/mol), but made no mention of the transition state structures leading to either the *E* or *Z* isomers in the insertion reaction.[11]

With little hard evidence in the literature available to rationalize the hydrophosphination mechanism present with the lanthanum-based catalysis reported herein, we propose a plausible catalytic cycle in line with the results above (Scheme 3). Two key details that required inclusion were the second order dependency on lanthanum and the *Z* stereoselectivity displayed by the kinetic product. To the first point, we propose that the lanthanum phosphido complex exists as a dimer, with diphenylphosphide ligands bridging the two lanthanum metal centers. The potential equilibrium between a lanthanum monomer and the catalytic lanthanum dimer present in the rate-determining step is consistent with the second order dependency on lanthanum. With our current evidence, we cannot speculate at what point a monomer is present within the entire reaction process. Mechanistically, the alkyne coordinates to one of the lanthanum centers, possibly disrupting one of the phosphido bridges. The coordination of alkenes and alkynes to lanthanides is well established in the rare-earth-metal polymerization literature.[17] Once coordinated to the lanthanum, the alkyne can undergo nucleophilic attack by a phosphide from the second lanthanum center, which effectively rationalizes the production of the *Z*-alkene as the kinetic product (Scheme 3, top right). Finally, protonolysis by diphenylphosphine yields the free *Z* isomer and regenerates the dimeric active species. The *Z* alkene is then subsequently isomerized to the thermodynamic *E* final product by the lanthanum phosphide active species. This isomerization could involve insertion of the product alkene into the La-P bond of the active catalyst, single bond rotation, and then subsequent β-phosphido elimination to produce the trans isomer (Scheme 4). This insertion-elimination sequence would allow equilibration between the *E*- and *Z*-isomers, ultimately leading to the more stable *E*-alkene products observed experimentally. Assuming insertion of the alkyne is more facile than insertion of the vinylphosphine due to sterics, hydrophosphination would be kinetically favored over

isomerization until the alkyne was almost completely consumed. The isolation of the kinetic *Z*-isomer under phosphine limiting conditions supports this process since the La-P bonds necessary for isomerization would not be present when the reaction runs out of phosphine substrate.



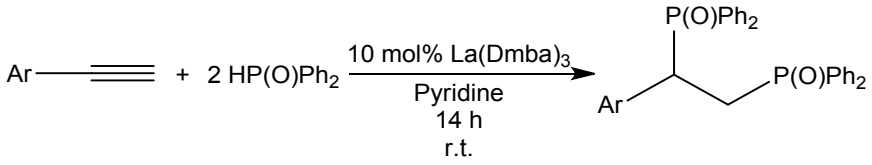
Scheme 3. Proposed catalytic cycle for lanthanum catalyzed hydrophosphination of alkynes

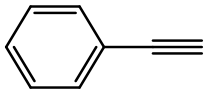
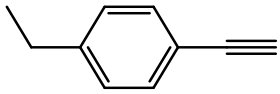
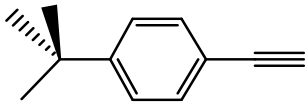
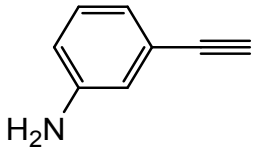


Scheme 4. Isomerization from the *Z* to *E* alkene could proceed via an insertion/deinsertion pathway.

Using the same conditions as hydrophosphination, $La(Dmba)_3$ was investigated as a precatalyst for the addition of diphenylphosphine oxide to internal and terminal alkynes. These hydrophosphinylation reactions proceeded with notable chemoselectivity. Intially, all the reactions were undertaken using the same conditions: 10 mol% catalytic loading and 1:1.3 alkyne to diphenylphosphine oxide in pyridine for 14 h. Interestingly, the reaction products were different depending on the nature of the alkyne tested. Terminal alkynes gave only double hydrophosphinylation products while internal alkynes resulted in single addition products. Therefore, the reactions of the terminal alkynes were repeated with a 1:2.3 alkyne to diphenylphosphine oxide ratio in order to optimize yield of the double addition products (Table 3), each of which was produced with 1,2-addition giving dppe-like compounds. Reduction of these doubly oxidized species to the dppe analogues could be undertaken using a variety of methods,[18] though this remains beyond the scope of the current report.

Table 3. Double Hydrophosphinylation of Terminal Alkynes



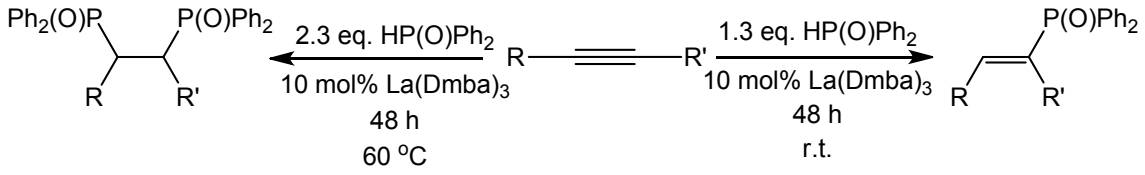
Entry	Alkyne	Yield(%)[a]
4a		95
4b		90
4c		90
4d		82

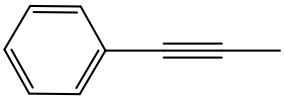
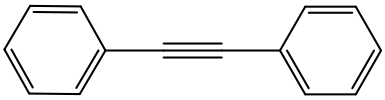
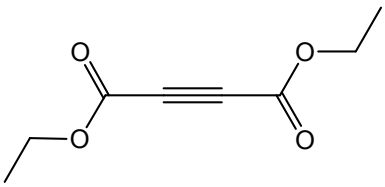
Catalytic reactions were carried out with $La(Dmba)_3$ (27 mg; 10 mol%), alkyne (0.5 mmol), and diphenylphosphine oxide (1.15 mmol) in pyridine (2 ml) for 14 h at room temperature. [a] Isolated yields.

At room temperature with 1.3 eq. of phosphine oxide, internal alkynes yielded single hydrophosphinylation products with only traces of the double hydrophosphinylation products detected. The reaction was completely regiospecific and highly stereoselective, yielding almost completely the *E* isomer in all cases. To induce complete conversion to the double addition

products using internal alkynes, the reactions required higher temperature (60 °C) and elongated reaction times (Table 4).

Table 4. Single and Double Hydrophosphinylation of Internal Alkynes



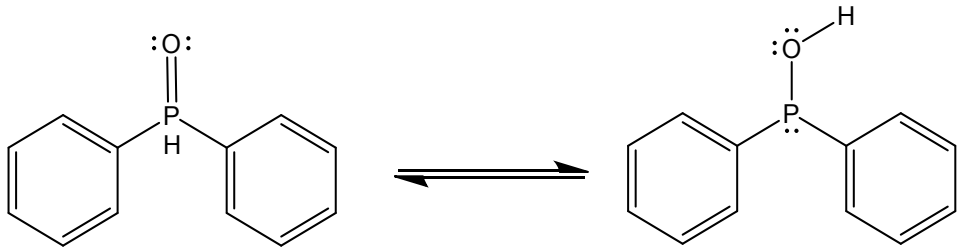
Yield(%)[a]	Alkyne	Yield(%)[a]	E:Z[b]
(**4e**) 80		(**5a**) 82	95:5
(**4f**) 60		(**5b**) 70	95:5
(**4g**) 60		(**5c**) 65	95:5

Catalytic reactions were carried out with La(Dmba)$_3$ (27 mg; 10 mol%), alkyne (0.5 mmol) and diphenylphosphine oxide (0.65 or 1.15 mmol) in pyridine (2 ml) for 48 h at room temperature or 60 °C. [a] Isolated yield. [b] Ratio determined by $^{31}P\{^{1}H\}$ NMR.

Unlike diphenylphosphine, which formed only monoaddition hydrophosphination products (Table 2), the production of double addition products in this case may be related to the ability of diphenylphosphine oxide to tautomerize (Scheme 5).[19] Since no double addition was observed in the case of hydrophosphination (Table 2), this tautomerization may play a crucial

role in the second addition, perhaps by reducing the steric strain at the metal center. On the other hand, we cannot discount the possibility that the difference in reactivity is simply a matter of activation by the electron withdrawing oxygen atom in this substrate. We know that during precatalyst activation, three equivalents of dimethylbenzylamine (HDmba) are liberated by reaction with diphenylphosphine oxide, creating the active catalyst in situ. Unlike the lanthanum trisphosphide used in the hydrophosphination reactions ($La(PPh_2)_3$), the diphenylphosphine oxide ligand can coordinate to lanthanum through either the phosphorus or the oxygen depending on the tautomer utilized. In order to look at this tautomerization effect experimentally, we undertook a series of stoichiometric reactions on an NMR scale in a J-Young tube (Figure 1). The precatalyst $La(Dmba)_3$ was first treated with three equivalents of diphenylphosphine in deuterated pyridine to produce $La(PPh_2)_3$, the hydrophosphination catalyst discussed above. The solution turned from clear to dark red with no precipitate observed and its $^{31}P\{^1H\}$ NMR spectrum was collected. Because both lanthanum isotopes are quadrupolar: ^{138}La (0.09% abundance, I = 5/2) and ^{139}La (99.91% abundance, I = 7/2), no phosphorus signal was detected for the resulting lanthanum phosphide complex.[20] To elaborate further, the nuclear spin of the lanthanum isotopes present resulted in broadening of the phosphorus signal to the point where it was lost in the baseline noise. Subsequently, an excess of diphenylphosphine oxide (six equivalents) was added to the solution, causing the reaction color to change from red to a colorless homogeneous solution. In this case, the corresponding $^{31}P\{^1H\}$ NMR spectrum showed three signals. A free diphenylphosphine resonance appeared at -40.0 ppm, a peak at 17.0 ppm corresponded to leftover excess diphenylphosphine oxide, and a new signal appeared at 87.2 ppm that we attribute to the activated $La(O\text{-}PPh_2)_3$ catalyst (Figure 1). Because the peak at 87.2 ppm was visible and not appreciably broadened, we believe this indicates coordination of the

phosphine oxide ligands via the oxygen donor atom, leaving the phosphorus atom further from the quadrupolar lanthanum center and thus visible in the ^{31}P NMR spectrum. A calcium complex of the O-bound Ph_2PO^- moiety was previously reported to have a ^{31}P NMR resonance at 89.6 ppm, well in line with that observed in our system.[21] We cannot discount the possibility that the observed peak at 87.2 ppm is an uncoordinated Ph_2PO^- anion, though this seems unlikely in the presence of the highly oxophilic La^{3+} ions. Moreover, a control experiment in which $HP(O)Ph_2$ was dissolved in pyridine showed no evidence for deprotonation by pyridine (see Supporting Information). This was unsurprising as the pKa of $HP(O)Ph_2$ has been reported as 20.6 (in DMSO)[22] and the pKb of pyridine is 8.77.[23] Utilizing these values, the approximate equilibrium constant for their acid-base reaction is around 1×10^{-15}.



Scheme 5. Tautomerization of diphenylphosphine oxide

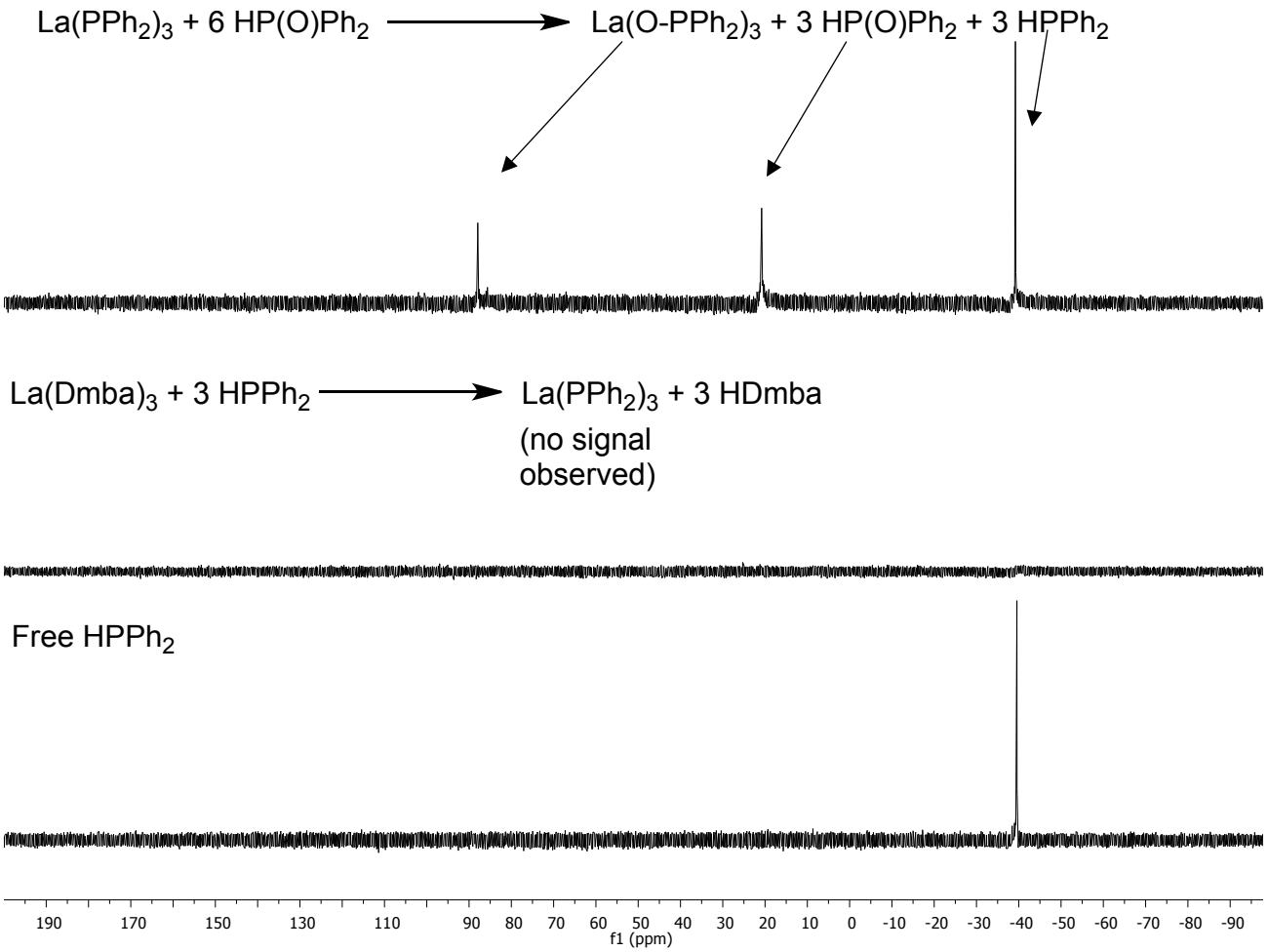
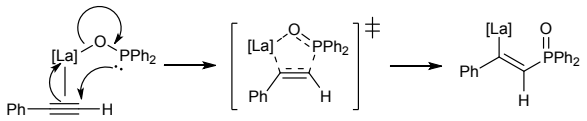


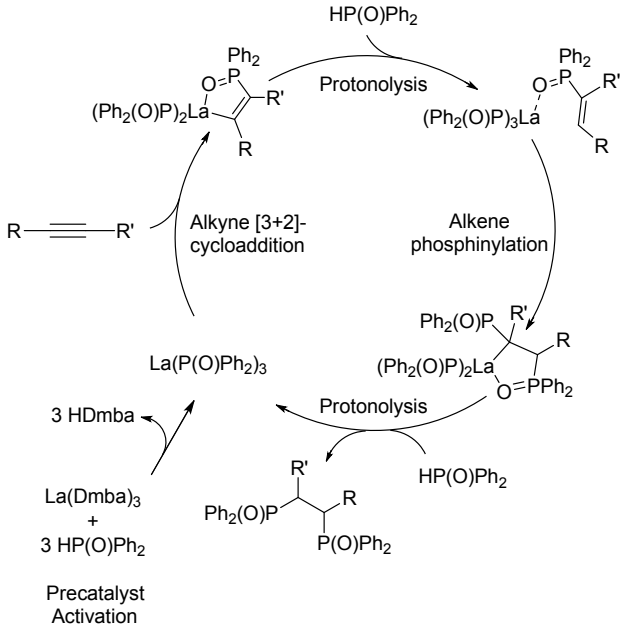
Figure 1. $^{31}P\{^{1}H\}$ NMR spectra in d_5-pyridine of reaction sequence displaying evidence for the tautomerization of phosphine oxide when coordinated to lanthanum

Mechanistically, stoichiometric reaction of the precatalyst with phosphine oxide leads to creation of the active catalyst in situ. Based on the NMR scale experiments above, this species is likely the pyridine solvated, O-bound lanthanum complex: $La(O\text{-}PPh_2)_3(py)_n$. The next step likely involves coordination of an alkyne to the La, but due to tautomerization of the phosphine oxide ligand, direct insertion would not lead to formation of a carbon-phosphorus bond. Rather, production of the putative insertion products likely occurs via a [3+2]-cycloaddition process (Scheme 6). A [3+2]-addition process such of this is also facilitated by the tautomerization as shown by the electron pushing arrows in Scheme 6. Catalysis then continues in a similar fashion

to the hydrophosphination catalytic cycle with protonolysis via another equivalent of diphenylphosphine oxide as shown in the full catalytic cycle (Scheme 7). As mentioned above, the mono-addition product can only be isolated in the case of internal alkynes, showing high regio- and stereoselectivity producing almost exclusively the *E* isomer. Given the oxophilicity of lanthanum and the ability of phosphine oxide to tautomerize, the intermediates likely have O-bound phosphine oxides, significantly reducing the steric bulk at the metal center. Since mono-addition products cannot be isolated with terminal alkynes, it is believed that the intermediate mono-addition alkene remains coordinated to the metal center. The greatly reduced steric congestion around the metal center then allows for rapid addition of another phosphine oxide moiety to the alkene unit, with final protonolysis by diphenylphosphine oxide yielding the double addition products (Scheme 7).



Scheme 6. Tautomerization of the phosphine oxide ligands leads to a [3+2] cycloaddition mechanism.



Scheme 7. Proposed catalytic cycle for lanthanum catalyzed mono- and double hydrophosphinylation of alkynes (pyridine solvation omitted for clarity).

Conclusions

We demonstrated the ability of $La(Dmba)_3$ to induce both hydrophosphination and hydrophosphinylation of alkynes. Interesting chemoselectivity was observed: the catalyst induced only mono-addition in hydrophosphination reactions but mono- and double addition in hydrophosphinylation reactions. Both mono-addition reactions showed high regioselectivity, where only anti-Markovnikov products were observed. In hydrophosphination, the stereoselectivity could be controlled depending on the reaction conditions employed. A brief investigation of the catalytic cycle suggested the formation of a dimeric lanthanum phosphide active catalyst and the formation of the Z isomer as the kinetic product, which then underwent isomerization to yield the thermodynamic E isomer. Control reactions showed that the presence of the active catalyst was imperative for the isomerization to occur.

Hydrophosphinylation reactions led directly to double addition products when using terminal alkynes; however, both mono- and double addition products could be isolated when using internal alkynes. Overall, we demonstrated a new pathway to mono- and bidentate phosphine and phosphine oxide ligands using relatively mild conditions with high chemo-, regio-, and stereoselectivity.

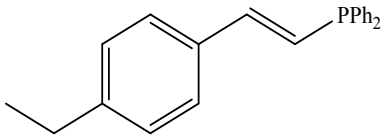
Experimental

Lanthanum tris(*N,N*-dimethylbenzylamine) ($La(Dmba)_3$) was synthesized as previously reported.[24] All acetylenes were purchased from Alfa Aesar or AK Scientific, dried over calcium hydride, filtered, freeze-pump-thawed three times, and stored in a nitrogen filled glovebox. All solvents were dried before use; diethyl ether, dichloromethane, and pentane were passed through columns of 4Å molecular sieves and degassed with nitrogen. Pyridine was purchased from Alfa Aesar, and dried over sodium metal, distilled under nitrogen, freeze-pump-thawed three times, and stored in a nitrogen filled glovebox. Diphenylphosphine oxide was purchased from Glass City Chemicals, stored in a glovebox, and used without further manipulations. Diphenylphosphine was synthesized by the reduction of chlorodiphenylphosphine with lithium aluminum hydride and stored in a glovebox.[25] All reactions were carried out in the glovebox under nitrogen atmosphere. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, and for air sensitive purposes, it was dried over calcium hydride, vacuum transferred, freeze-pump-thawed three times, and stored over molecular sieves in a nitrogen filled glovebox. All ^{1}H and ^{13}C NMR spectra were collected on a 600 MHz Bruker Avance III spectrometer at 599.9 and 150.8 MHz, respectively, and referenced to the residual solvent peaks of chloroform at 7.26 and 77.3 ppm. All ^{31}P NMR spectra were collected on a 400 MHz Varian VXRS NMR spectrometer at 161.9 MHz and externally referenced to 0.00 ppm with 5% H_3PO_4 in D_2O. Infrared spectra

were collected on a PerkinElmer Frontier spectrometer with Pike miracle ATR. High resolution mass spectra were determined at the Department of Chemistry and Biochemistry, University of Toledo, OH, USA, using a Waters Synapt high-definition mass spectrometer (HDMS) equipped with a nano-ESI source.

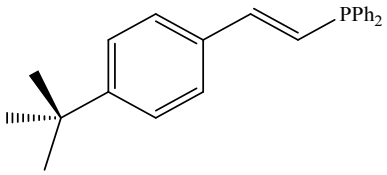
Hydrophosphination of Alkynes (*E*-isomer).

In the glovebox, an oven dried Schlenk tube was charged with $La(Dmba)_3$ (13.5 mg; 5 mol%) and pyridine (1 ml), resulting in an orange solution. Diphenylphosphine (0.8 mmol, 139.2 µl) was measured with a micropipette and added to the $La(Dmba)_3$, resulting in a deep red solution after 5 minutes. Acetylene (0.5 mmol) was then dissolved in pyridine (1 ml) and added to the lanthanum phosphide solution resulting in a color change to a pale yellow or colorless solution. The Schlenk tube was removed from the glovebox and the reaction was stirred for 12-48 h at room temperature. The solvent was then removed under vacuum and the products were washed with cold pentane (2x5 ml) under air sensitive conditions.[26] Clean products were afforded by recrystallization from diethyl ether. Hydrophosphination products **2a**,[27] **2e**,[27] and **2f**[28] were identified by comparison to previously reported NMR spectral data. Note that the ^{1}H NMR of **2f** as previously reported seems incorrect so we have included our data herein for comparison.

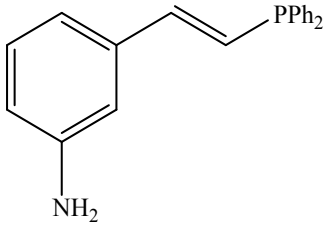


(**2b)** Off white solid, 130.0 mg (82%), M.P: 110-113°C. ^{1}H NMR ($CDCl_3$): δ 7.76-7.73 (m, 3H), 7.55-7.52 (m, 2H), 7.48-7.44 (m, 6H), 7.36-7.29 (m, 2H), 7.21 (d, $^3J_{H-H}$= 8.0Hz, 2H), 6.77 (dd, $^3J_{H-H}$= 20.0Hz, $^2J_{H-P}$= 17.0Hz, 1H), 2.66 (q, $^3J_{H-H}$= 7.6Hz, 2H), 1.23 (t, $^3J_{H-H}$= 7.6Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.5 (d, J_{C-P} = 4.0Hz), 146.7, 133.4, 132.7 (d, J_{C-P} = 20.0Hz), 131.8 (d, J_{C-P} = 2.2Hz), 131.6 (d, J_{C-P} = 9.8Hz), 128.9 (d, J_{C-P} = 12.0Hz), 128.7,

128.1, 117.8 (d, J_{C-P} = 18.0Hz), 29.0, 15.7. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -10.6. IR (cm^{-1}): 2963.1 (m), 1606.5 (m), 1523.3 (w), 1511.1 (w), 1470.0 (w), 1436.2 (m), 1349.8 (w), 1310.3 (m), 1179.0 (s), 1137.6 (m), 1118.3 (s), 1110.1 (s), 1060.3 (w), 1047.0 (w), 1012.0 (m), 810.5 (s), 769.1 (m), 742.0 (s), 720.2 (m), 707.4 (m), 691.4 (s), 594.0 (m), 523.8 (s), 497.4 (m), 462.0 (m). $HRMS_{calc}$ for $C_{22}H_{22}OP$ $[M+H+O]^{+}$:[29] 333.1408, $HRMS_{meas}$: 333.1422.

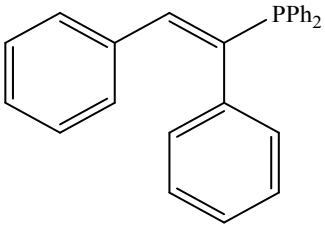


(**2c**) White solid, 146.5 mg (85%). ^{1}H NMR ($CDCl_3$): δ 7.76-7.73 (m, 4H), 7.55-7.52 (m, 2H), 7.48-7.45 (m, 6H), 7.41-7.39 (m, 2H), 7.29-7.27 (m, 1H), 6.77 (dd, $^{3}J_{H-H}$ = 22.3Hz, $^{2}J_{H-P}$ = 17.0Hz, 1H), 1.32 (s, 9H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 153.9, 147.7 (d, J_{C-P} = 3.0Hz), 133.7, 133.0, 132.7 (d, J_{C-P} = 18.1Hz), 132.1 (d, J_{C-P} = 3.0Hz), 131.7 (d, J_{C-P} = 10.0Hz), 128.9 (d, J_{C-P} = 12.1Hz), 128.3 (d, J_{C-P} = 12.1Hz), 127.9, 126.1, 118.7, 35.1, 31.4. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -10.7. $HRMS_{calc}$ for $C_{24}H_{26}OP$ $[M+H+O]^{+}$:[29] 361.1721, $HRMS_{meas}$: 361.1724.

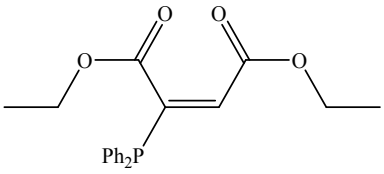


(**2d**) Off white solid, 111.0 mg (73%), M.P: 116-122°C. ^{1}H NMR ($CDCl_3$): δ 7.47-7.44 (m, 4H), 7.34-7.31 (m, 6H), 7.12-7.10 (m, 2H), 6.91-6.85 (m, 2H), 6.61-6.60 (m, 1H), 6.42 (dd, $^{3}J_{H-H}$ = 13.0Hz, $^{2}J_{H-P}$ = 3.0Hz, 1H), 3.61 (br s, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 146.4, 144.6 (d, J_{C-P} = 19.0Hz), 139.8 (d, J_{C-P} = 10.0Hz), 138.2 (d, J_{C-P} = 2.3Hz), 133.3 (d, J_{C-P} = 19.0Hz), 129.8, 129.5 (d, J_{C-P} = 16.0Hz), 129.3, 129.0, 128.9 (d, J_{C-P} = 6.0Hz), 128.8 (d, J_{C-P} = 6.0Hz), 128.7, 120.5 (d, J_{C-P} = 8.0Hz), 116.3 (d, J_{C-P} = 8.0Hz), 115.3. $^{31}P\{^{1}H\}$

NMR ($CDCl_3$): δ -10.7. IR (cm^{-1}): 2962.0 (m), 2156.3 (w), 1580.5 (w), 1516.6 (m), 1434.2 (w), 1345.8 (w), 1257.7 (s), 1224.2 (w), 1070.1 (s), 1056.3 (m), 1009.5 (s), 931.0 (w), 863.1 (m), 847.7 (m), 786.1 (s), 692.6 (s), 594.0 (w), 471.1 (s). $HRMS_{calc}$ for $C_{20}H_{18}NOP$ $[M+O]^{+}$:[29] 319.1126, $HRMS_{meas}$: 319.1122.



(**2f**)[28] White solid, 118.5 mg (65%). ^1H NMR ($CDCl_3$): δ 7.68-7.65 (m, 4H), 7.60 (d, $^3J_{H-P}$ = 21.0Hz, 1H), 7.52-7.49 (m, 2H), 7.40 (td, $^3J_{H-H}$ = 7.8Hz, $^4J_{H-P}$ = 2.8Hz, 4H), 7.22-7.16 (m, 4H), 7.13 (t, $^3J_{H-H}$ = 7.8Hz, 2H), 7.04 (d, $^3J_{H-H}$ = 7.5Hz, 2H), 6.91 (d, $^3J_{H-H}$ = 6.5Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 150.1, 143.3 (d, J_{C-P} = 9.0Hz), 135.9, 135.8 (d, J_{C-P} = 9.0Hz), 135.3, 135.1 (d, J_{C-P} = 17.0Hz), 132.6 (d, J_{C-P} = 9.0Hz), 132.1 (d, J_{C-P} = 2.0Hz), 131.6, 130.9, 130.5, 130.2 (d, J_{C-P} = 4.0Hz), 129.1, 129.0, 128.5, 128.4 (d, J_{C-P} = 2.0Hz), 127.8, 124.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.5.

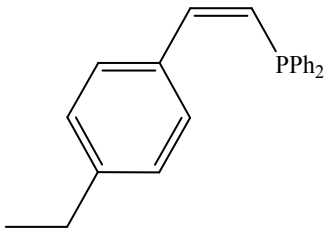


(**2g**) Yellow solid, 107.0 mg (60%). M.P: 140-146°C. ^1H NMR ($CDCl_3$): δ 7.72-7.69 (m, 2H), 7.35-7.34 (m, 3H), 7.30-7.26 (m, 3H), 7.20 (t, $^3J_{H-H}$ = 7.8Hz, 2H), 4.16 (d, $^3J_{H-P}$ = 7.0Hz, 1H), 3.98-3.97 (m, 1H), 3.88-3.86 (m, 1H), 3.54-3.52 (m, 1H), 3.44-3.41 (m, 1H), 0.83 (t, $^3J_{H-H}$ = 7.4Hz, 3H), 0.71 (t, $^3J_{H-H}$ = 7.4Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.9, 150.2, 135.1 (d, J_{C-P} = 11.0Hz), 134.6 (d, J_{C-P} = 13.0Hz), 134.2 (d, J_{C-P} = 17.2Hz), 133.9 (d, J_{C-P} = 10.0Hz), 129.7 (d, J_{C-P} = 11.0Hz), 128.8 (d, J_{C-P} = 11.0Hz), 60.7 (d, J_{C-P} = 2.0Hz), 46.6 (d, J_{C-P} = 2.0Hz), 13.8, 13.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 3.6. IR (cm^{-1}): 3053.5 (m), 2981.7 (m), 2283.1 (w), 1720.1 (s), 1584.7 (m), 1537.4 (w), 1478.5 (m), 1434.3 (s), 1240.5 (m), 1220.4 (w), 1189.9

(m), 1150.1 (m), 1090.1 (m), 1069.2 (w), 1025.7 (s), 999.1 (w), 910.6 (w), 888.6 (m), 853.0 (w), 795.6 (s), 740.8 (m), 692.6 (s), 647.2 (m), 617.8 (w), 561.8 (w), 483.8 (w), 471.9 (w), 455.0 (w). $HRMS_{calc}$ for $C_{20}H_{22}O_5P$ $[M+H+O^+]$:[29] 373.1205, $HRMS_{meas}$:373.1207.

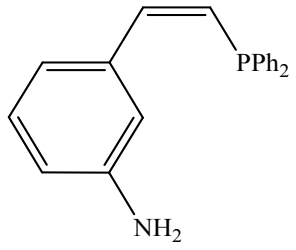
Hydrophosphination of Alkynes (*Z*-isomer).

In the glovebox, an oven dried Schlenk tube was charged with $La(Dmba)_3$ (13.5 mg; 5 mol%) and pyridine (1 ml), resulting in an orange solution. Diphenylphosphine (0.5 mmol, 93 µl) was measured with a micropipette and added to the $La(Dmba)_3$ resulting in a deep red solution after 5 minutes. Acetylene (0.8 mmol) was then dissolved in pyridine (1 ml) and added to the lanthanum phosphide solution resulting in a color change to a pale yellow or colorless solution. The Schlenk tube was removed from the glovebox and the reaction was stirred for 12 h at room temperature. The solvent was then removed under vacuum and the products were extracted with diethyl ether (2x5 ml) under air sensitive conditions. Diethyl ether was then removed under reduced pressure to afford clean product. Hydrophosphination product **2a'**[8, 12, 30] was identified by comparison to previously reported NMR spectral data.



(**2b'**) Off-white solid, 134.5 mg (85%), M.P: 100-110°C. ^1H NMR ($CDCl_3$): δ 7.47-7.43 (m, 5H), 7.38 (d, $^3J_{H-H}$ = 12.6Hz, 1H), 7.35-7.31 (m, 8H), 7.16 (d, $^3J_{H-H}$ = 8.0Hz, 1H), 6.40 (dd, $^3J_{H-H}$ = 12.6Hz, $^2J_{H-P}$ = 3.0Hz, 1H), 2.63 (q, $^3J_{H-H}$ = 7.6Hz, 2H), 1.22 (t, $^3J_{H-H}$ = 7.6Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.6, 144.3 (d, J_{C-P} = 19.0Hz), 139.6 (d, J_{C-P} = 9.0Hz), 134.5 (d, J_{C-P} = 2.0Hz), 132.8 (d, J_{C-P} = 18.6Hz), 129.7 (d, J_{C-P} = 8.0Hz), 128.6 (d, J_{C-P} =

6.0Hz), 128.6, 128.3 (d, J_{C-P} = 15.0Hz), 127.8, 28.9, 15.7. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -23.7. IR(cm^{-1}): 3052.5 (w), 2930.0 (w), 1587.1 (w), 1508.0 (m), 1455.1 (w), 1432.2 (m), 1333.2 (w), 1303.5 (w), 1184.9 (w), 1154.5 (w), 1092.0 (m), 1067.2 (m), 1050.9 (w), 1025.8 (m), 971.9 (m), 912.2 (m), 845.6 (s), 826.9 (s), 737.2 (s), 695.7 (s), 655.9 (m). $HRMS_{calc}$ for $C_{22}H_{22}P$ [$M+H^+$]: 317.1459, $HRMS_{meas}$: 317.1464.

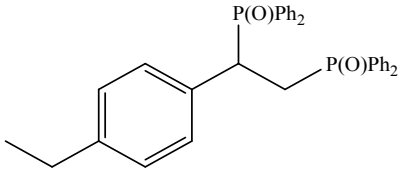


(**2d'**) Pale yellow solid, 121.3 mg (80%), M.P: 95-100°C. ^{1}H NMR ($CDCl_3$): δ 7.45-7.43 (m, 6H), 7.35-7.31 (m, 8H), 6.63 (dd, $^{3}J_{H-H}$ = 12.6Hz, $^{3}J_{H-P}$ = 1.4Hz, 1H), 6.41 (dd, $^{3}J_{H-H}$ = 12.6Hz, $^{2}J_{H-P}$ = 3.0Hz, 1H), 3.68 (br s, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 146.1, 144.3 (d, J_{C-P} = 19.0Hz), 139.5 (d, J_{C-P} = 9.4Hz), 132.8 (d, J_{C-P} = 19.0Hz), 129.5, 129.1, 128.6 (d, J_{C-P} = 9.0Hz), 118.5, 116.5 (d, J_{C-P} = 8.4Hz), 116.0. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -25.2. IR (cm^{-1}): 3142.5 (w), 2990.9 (m), 1590.1 (w), 1500.0 (m), 1443.3 (w), 1400.2 (m), 1299.9 (m), 1154.8 (w), 1144.4 (w), 1091.9 (w), 1077.1 (m), 1050.9 (w), 1049.3 (m), 980.1 (w), 900.1 (m), 845.6 (s), 823.2 (s), 776.2 (s). $HRMS_{calc}$ for $C_{20}H_{19}NP$ [$M+H^+$]: 304.1255, $HRMS_{meas}$: 304.1272.

Double Hydrophosphinylation of Alkynes.

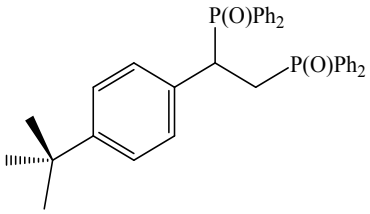
In the glovebox, an oven dried vial was charged with $La(Dmba)_3$ (27 mg; 10 mol%) and pyridine (2 ml) resulting in an orange solution. Diphenylphosphine oxide (232.5 mg; 1.15 mmol) was added to the $La(Dmba)_3$ solution, resulting immediately in a clear and colorless solution. Acetylene (0.5 mmol) was then added to the lanthanum phosphinyl oxide solution. The vial was then removed from the glovebox and the reaction was stirred for 12-48 h at room temperature or 60°C. The solvent was removed under vacuum and the products were washed with diethyl ether

(2x5 ml) under ambient conditions, filtered, and recrystallized from dichloromethane (5 ml) to afford clean product. Hydrophosphination products **4a**[31] and **4f**[32] were identified by comparison to previously reported NMR spectral data.

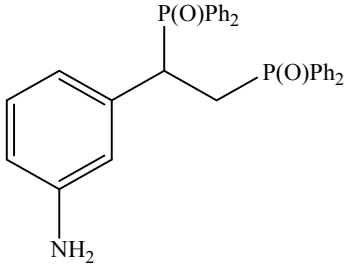


(**4b**) White solid, 240.5 mg (90%), M.P: 206°C dec. ^{1}H NMR ($CDCl_3$): δ 8.05-8.02 (m, 2H), 7.59-7.50 (m, 5H), 7.44-7.40 (m, 2H), 7.36-7.25 (m, 6H), 7.19-7.14 (m, 3H), 7.04 (td, $^{3}J_{H-H}$ = 5.4Hz, $^{4}J_{H-P}$ = 1.0Hz, 2H), 6.97 (d, $^{3}J_{H-H}$ = 7.6Hz, 2H), 6.63 (d, $^{3}J_{H-H}$ = 7.6Hz, 2H), 4.28-4.23 (m, 1H), 3.15-3.10 (m, 1H), 2.84-2.77 (m, 1H), 2.37 (q, $^{3}J_{H-H}$ = 7.6Hz, 2H), 1.05 (t, $^{3}J_{H-H}$ = 7.6Hz, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 135.0, 134.4, 133.2 (d, J_{C-P} = 2.5Hz), 132.7 (d, J_{C-P} = 10.0Hz), 132.5 (d, J_{C-P} = 16.0Hz), 132.2 (d, J_{C-P} = 3.0Hz), 132.1 (d, J_{C-P} = 8.6Hz), 131.9, 131.8 (d, J_{C-P} = 6.0Hz), 131.7, 131.4 (d, J_{C-P} = 8.6Hz), 131.3 (d, J_{C-P} = 8.6Hz), 130.8 (d, J_{C-P} = 10.0Hz), 130.6 (d, J_{C-P} = 6.0Hz), 129.6 (d, J_{C-P} = 11.0Hz), 129.5 (d, J_{C-P} = 13.0Hz), 129.2 (d, J_{C-P} = 11.0Hz), 128.8 (d, J_{C-P} = 13.0Hz), 128.6 (d, J_{C-P} = 12.0Hz), 128.5 (d, J_{C-P} = 12.0Hz), 128.4, 127.9, 39.3 (dd, J_{C-P} = 66.0Hz, J_{C-P} = 3.5Hz), 30.7 (d, J_{C-P} = 69.0Hz), 28.9, 16.2. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 38.0 (d, $^{3}J_{P-P}$ = 47.0Hz), 32.6 (d, $^{3}J_{P-P}$ = 47.0Hz). IR (cm^{-1}): 3054.4 (w), 2966.0 (w), 2901.9 (w), 1671.2 (w), 1590.8 (w), 1513.1 (w), 1483.6 (w), 1436.1 (m), 1310.6 (w), 1181.5 (m), 1128.8 (s), 1069.8 (m), 1045.5 (s), 1021.0 (s), 996.6 (m), 948.2 (m), 887.8 (m), 839.7 (m), 796.4

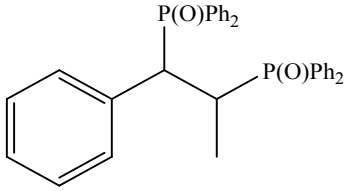
(w), 742.8 (m), 724.4 (s), 690.0 (m), 556.1 (s), 517.8 (s), 509.1 (s). $HRMS_{calc}$ for $C_{34}H_{33}O_2P_2$ $[M+H^+]$: 535.1956, $HRMS_{meas}$: 535.1965.



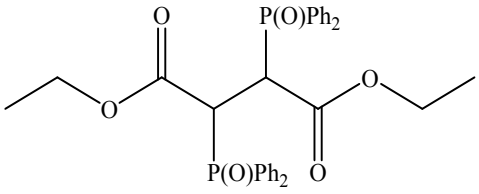
(**4c**) White solid, 253.0 mg (90%), M.P: >250°C. ^1H NMR ($CDCl_3$): δ 8.06-8.04 (m, 2H), 7.73-7.68 (m, 1H), 7.57-7.53 (m, 5H), 7.43 (td, $^3J_{H-H}$ = 7.3Hz, $^4J_{H-H}$ = 1.3Hz , 1H), 7.36-7.34 (m, 2H), 7.30-7.29 (m, 2H), 7.25-7.24 (m, 1H), 7.17-7.11 (m, 4H), 7.05-7.02 (m, 2H), 6.95 (d, $^3J_{H-H}$ = 7.6Hz, 2H), 6.81 (d, $^3J_{H-H}$ = 8.2Hz, 2H), 4.27-4.22 (m, 1H), 3.17-3.12 (m, 1H), 2.84-2.77 (m, 1H), 1.14 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.5, 132.1, 131.8, 131.7 (d, J_{C-P} = 8.4Hz), 131.4, 131.1, 130.9 (d, J_{C-P} = 9.1Hz), 130.8 (d, J_{C-P} = 3.1Hz), 130.7 (d, J_{C-P} = 9.5Hz), 130.6 (d, J_{C-P} = 13.0Hz), 130.5 (d, J_{C-P} = 13.0Hz), 130.2 (d, J_{C-P} = 9.5Hz), 129.7 (d, J_{C-P} = 5.5Hz), 129.1 (d, J_{C-P} = 11.0Hz), 128.9 (d, J_{C-P} = 13.0Hz), 128.6 (d, J_{C-P} = 12.0Hz), 127.8 (d, J_{C-P} = 12.0Hz), 124.7, 38.7 (dd, J_{C-P} = 66.0Hz, J_{C-P} = 3.3Hz), 34.0, 31.2, 30.0 (d, J_{C-P} = 69.0Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.5 (d, $^3J_{P-P}$ = 47.0Hz), 31.0 (d, $^3J_{P-P}$ = 47.0Hz). IR (cm^{-1}): 3054.2 (w), 2965.1 (w), 2937.1 (w), 1591.8 (w), 1511.4 (w), 1484.0 (w), 1437.8 (m), 1365.5 (w), 1339.8 (w), 1264.8 (w), 1182.1 (s), 1119.7 (s), 1102.8 (m), 1071.8 (w), 1045.3 (m), 1021.8 (m), 997.1 (w), 887.2 (w), 839.0 (m), 790.1 (w), 773.0 (w), 762.8 (w), 746.0 (m), 729.3 (m), 720.2 (s), 692.9 (s), 661.2 (w), 574.5 (w), 558.9 (w), 535.8 (w). $HRMS_{calc}$ for $C_{36}H_{37}O_2P_2$ $[M+H^+]$: 563.2269, $HRMS_{meas}$: 563.2259.



(**4d**) White solid, 216.4 mg (83%), M.P: >250°C. ^{1}H NMR ($CDCl_3$): δ 8.03-7.99 (m, 2H), 7.71-7.67 (m, 1H), 7.54-7.48 (m, 5H), 7.43-7.39 (m, 1H), 7.37-7.32 (m, 6H), 7.25-7.20 (m, 1H), 7.17-7.10 (m, 4H), 6.58 (t, $^{3}J_{H-H}$ = 7.8Hz, 1H), 6.48-6.45 (m, 2H), 6.17 (d, $^{3}J_{H-H}$ = 7.8Hz, 1H), 4.18-4.13 (m, 1H), 3.30 (bs, 2H), 3.12-3.06 (m, 1H), 2.81-2.74 (m, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 135.4 (d, J_{C-P} = 6.0Hz), 134.6, 134.0, 132.8 (d, J_{C-P} = 2.3Hz), 132.6 (d, J_{C-P} = 8.5Hz), 132.2 (d, J_{C-P} = 2.3Hz), 132.0, 131.8 (d, J_{C-P} = 2.3Hz), 131.7 (d, J_{C-P} = 8.5Hz), 131.5 (d, J_{C-P} = 2.3Hz), 131.4, 131.3, 131.1 (d, J_{C-P} = 9.0Hz), 130.9 (d, J_{C-P} = 10.0Hz), 130.4 (d, J_{C-P} = 9.0Hz), 129.4, 129.2 (d, J_{C-P} = 11.5Hz), 129.1 (d, J_{C-P} = 13.0Hz), 128.8 (d, J_{C-P} = 11.5Hz), 128.5 (d, J_{C-P} = 10.0Hz), 128.1 (d, J_{C-P} = 11.5Hz), 127.9 (d, J_{C-P} = 13.0Hz), 120.9 (d, J_{C-P} = 6.0Hz), 116.8 (d, J_{C-P} = 6.0Hz), 114.3 (d, J_{C-P} = 2.0Hz), 39.2 (dd, J_{C-P} = 66.0Hz, J_{C-P} = 3.0Hz), 30.2 (d, J_{C-P} = 69.0Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 36.3 (d, $^{3}J_{P-P}$ = 47.0Hz), 31.1 (d, $^{3}J_{P-P}$ = 47.0Hz). IR(cm^{-1}): 3053.9 (w), 2933.9 (w), 1604.3 (w), 1484.7 (m), 1464.8 (w), 1437.0 (m), 1310.3 (w), 1257.5 (w), 1181.7 (s), 1166.0 (m), 1118.5 (m), 1102.7 (m), 1072.9 (w), 1047.4 (w), 1029.0 (w), 997.0 (w), 879.4 (w), 843.8 (w), 795.1 (w), 729.5 (s), 690.4 (s), 618.2 (w), 607.9 (w), 539.8 (w), 498.2 (w), 481.1 (w), 460.4 (w). $HRMS_{calc}$ for $C_{32}H_{30}NO_2P_2$ [$M+H^+$]: 522.1752, $HRMS_{meas}$: 522.1765.



(**4e**) White solid, 208.0 mg (80%), M.P: > 250°C. ^{1}H NMR ($CDCl_3$): δ 8.12-8.09 (m, 2H), 7.72-7.69 (m, 2H), 7.55-7.49 (m, 3H), 7.40-7.33 (m, 5H), 7.23-7.18 (m, 6H), 7.08 (t, $^{3}J_{H-H}$ = 7.4Hz, 2H), 7.02-6.97 (m, 4H), 6.65 (t, $^{3}J_{H-H}$ = 6.8Hz, 1H), 4.33-4.29 (m, 1H), 3.61-3.58 (m, 1H), 1.19 (dd, $^{3}J_{H-P}$ = 17.3Hz, $^{3}J_{H-H}$ = 7.4Hz, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 136.1 (d, J_{C-P} = 5.5Hz), 135.0 (d, J_{C-P} = 45.6Hz), 133.8, 133.6 (d, J_{C-P} = 20.0Hz), 133.5, 133.1 (d, J_{C-P} = 4.5Hz), 132.9, 131.6 (dd, J_{C-P} = 35.0Hz, J_{C-P} = 2.0Hz), 131.0 (d, J_{C-P} = 8.4Hz), 130.8 (d, J_{C-P} = 8.4Hz), 130.7 (d, J_{C-P} = 8.4Hz), 130.6 (d, J_{C-P} = 2.0Hz), 130.5 (d, J_{C-P} = 9.0Hz), 129.1 (d, J_{C-P} = 11.4Hz), 128.8 (d, J_{C-P} = 11.4Hz), 127.9 (d, J_{C-P} = 12.0Hz), 126.9 (d, J_{C-P} = 2.0Hz), 45.4 (d, J_{C-P} = 65.0Hz), 36.8 (d, J_{C-P} = 68.0Hz), 15.6-15.5 (m). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 34.6 (d, $^{3}J_{P-P}$ = 40.5Hz), 27.4 (d, $^{3}J_{P-P}$ = 40.5Hz). IR(cm^{-1}): 3059.2 (w), 1592.1 (w), 1486.1 (w), 1437.0 (m), 1175.0 (s), 1132.0 (m), 1116.8 (m), 1101.1 (w), 1072.3 (w), 1047.0 (m), 1022.1 (m), 998.2 (w), 926.3 (w), 900.2 (w), 841.3 (w), 779.3 (m), 749.2 (m), 715.9 (s), 693.3 (s), 618.4 (w), 550.3 (m), 524.3 (w), 502.7 (w), 489.0 (w), 466.5 (w). $HRMS_{calc}$ for $C_{33}H_{31}O_2P_2$ [$M+H^+$]: 521.1799, $HRMS_{meas}$: 521.1804.

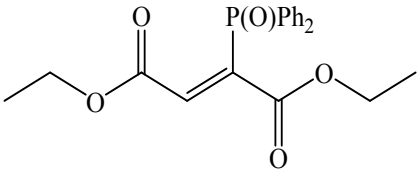


(**4g**) Orange solid, 172.4 mg (60%). M.P: 186°C dec. ^{1}H NMR ($CDCl_3$): δ 8.09-8.05 (m, 4H), 7.68-7.65 (m, 4H), 7.58-7.52 (m, 6H), 7.44 (t, $^{3}J_{H-H}$ = 7.0Hz, 3H), 7.35 (t, $^{3}J_{H-H}$ = 7.0Hz, 3H), 4.71 (d, $^{2}J_{H-P}$= 4.6Hz, 2H), 3.44-3.41 (m, 2H), 3.25-3.22 (m, 2H), 0.63 (t, $^{3}J_{H-H}$ = 7.1Hz, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 207.3, 166.1, 132.4 (d, J_{C-P} = 3.8Hz), 132.3 (d, J_{C-P} = 4.7Hz), 132.2, 131.4 (vt,^{33} J_{C-P} = 4.5Hz), 128.9 (vt,^{33} J_{C-P} = 5.9Hz), 128.2 (vt,^{33} J_{C-P} = 6.2Hz), 61.6, 49.1-48.8 (m), 31.2, 13.3. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 37.2. IR(cm^{-1}): 3060.8 (w), 2982.5 (w), 1720.0 (s), 1589.6 (w), 1482.3 (w), 1437.1 (m), 1391.8 (w), 1367.1 (w), 1241.6 (m), 1196.2 (s), 1140.3 (s), 1112.8 (m), 1098.5 (m), 1071.8 (w), 1029.8 (m), 998.1 (w), 860.6 (w), 806.6 (m), 756.4 (m), 747.7 (m), 722.1 (s), 700.9 (s), 619.1 (w), 610.1 (w), 586.1 (w), 506.3 (w), 486.4 (w), 472.9 (w). $HRMS_{calc}$ for $C_{32}H_{33}O_6P_2$ [$M+H^+$]: 575.1752, $HRMS_{meas}$: 575.1759.

Single Hydrophosphinylation of Alkynes.

In the glovebox, an oven dried vial was charged with $La(Dmba)_3$ (27 mg; 10 mol%) and pyridine (2 ml) resulting in an orange solution. Diphenylphosphine oxide (116.2 mg; 0.65 mmol) was added to the $La(Dmba)_3$, resulting immediately in a clear and colorless solution. Acetylene (0.5 mmol) was then added to the lanthanum phosphinyl oxide solution. The vial was removed from the glovebox and the reaction was stirred for 48 h at room temperature. The solvent was then removed under vacuum and the products were extracted with diethyl ether (2x5 ml) under ambient conditions, filtered, and recrystallized from dichloromethane (5 ml) to afford clean

product. Hydrophosphination products **5a**[34] and **5b**[34-35] were identified by comparison to previously reported NMR spectral data.



(**5c**) Orange solid, 121 mg (65%). M.P.: 170-174°C. ^{1}H NMR ($CDCl_3$): δ 8.07-8.04 (m, 2H), 7.66-7.63 (m, 2H), 7.59-7.53 (m, 3H), 7.42 (t, $^{3}J_{H-H}$ = 7.7Hz, 1H), 7.33 (t, $^{3}J_{H-H}$ = 7.3Hz, 2H), 4.68 (d, $^{3}J_{H-P}$ = 4.5Hz, 1H), 3.50-3.46 (m, 1H), 3.41-3.38 (m, 2H), 3.23-3.20 (m, 1H), 1.38-1.25 (m, 3H), 0.61 (t, $^{3}J_{H-H}$ = 7.1Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 168.1, 132.9 (d, J_{C-P} = 3.0Hz), 132.4 (d, J_{C-P} = 3.0Hz), 131.0 (d, J_{C-P} = 9.5Hz), 130.8 (d, J_{C-P} = 9.5Hz), 129.5 (d, J_{C-P} = 12.4Hz), 128.1 (d, J_{C-P} = 15.0Hz), 14.3, 13.3. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 30.0. IR(cm^{-1}): 2962.5 (s), 2015.2 (m), 1726.7 (s), 1676.6 (m), 1589.0 (m), 1560.9 (w), 1525.9 (w), 1494.6 (w), 1436.6 (w), 1424.5 (m), 1381.6 (w), 1257.8 (s), 1221.1 (m), 1084.6 (s), 1058.5 (s), 1012.2 (s), 896.5 (w), 862.2 (w), 845.4 (m), 792.9 (s), 760.3 (m), 744.0 (w), 712.8 (m), 691.3 (s), 582.9 (w), 557.4 (w), 550.8 (w), 482.6 (m). $HRMS_{calc}$ for $C_{20}H_{22}O_5P$ [$M+H^+$]: 373.1205, $HRMS_{meas}$: 373.1224.

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Notes. The authors declare no competing financial interest.

Supporting Information: NMR spectra of all new compounds, an integrated ^{31}P{^{1}H} NMR spectrum from Figure 1, a control reaction between $HOPPh_2$ and pyridine, and kinetics data supporting reaction order in catalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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