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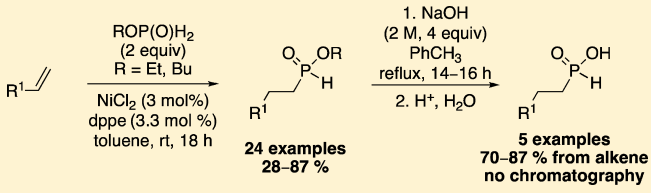
Hydrophosphinylation of Unactivated Terminal Alkenes Catalyzed by Nickel Chloride

Stéphanie Ortial, Henry C. Fisher, and Jean-Luc Montchamp*

Department of Chemistry, Box 298860, Texas Christian University, Fort Worth, Texas 76129, United States

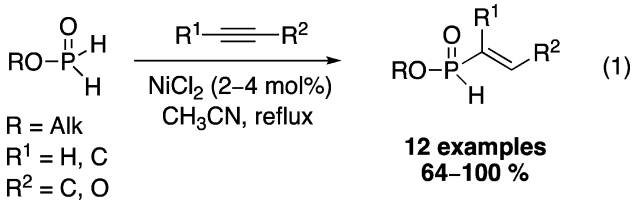
Supporting Information

ABSTRACT: The room-temperature hydrophosphinylation of unactivated monosubstituted alkenes using phosphinates ($ROP(O)H_2$) and catalytic $NiCl_2$ in the presence of dppe is described. The method is competitive with prior palladium-catalyzed reactions and uses a much cheaper catalyst and simple conditions. The scope of the reaction is quite broad in terms of unactivated terminal olefins, proceeds at room temperature, often avoids chromatographic purification, and allows one-pot conversion to various organophosphorus compounds.



INTRODUCTION

Organophosphorus compounds constitute an important class of industrial and fine chemicals because of their properties in flame-retardants, extractants, agrochemicals, ligands used in numerous metal-catalyzed reactions, pharmaceuticals, etc.[1] Addition reactions are intrinsically atom-economical because formation of byproducts is avoided. As a result, various methodologies for the addition of phosphorus reagents to alkenes and alkynes have been reported.[2] Our own interest in this area focuses on the addition chemistry of phosphinates ($ROP(O)H_2$)[3,4] and *H*-phosphinates ($R^1P(O)(OR)H$).[5] Importantly, phosphinates provide a more environmentally friendly alternative to phosphorus trichloride, the intermediate commonly employed in organophosphorus synthesis.[6] Like PCl_3, phosphinates are derived industrially from elemental phosphorus; however, they avoid the wasteful use of chlorine. Another advantage of phosphinates over other reagents such as *H*-phosphonates[7] is the synthetic flexibility *H*-phosphinates offer in accessing various functionalities.[6] The addition of phosphinates to unsaturated hydrocarbons could be industrially relevant, whereas currently only phosphine PH_3 is employed for this purpose.[8] Conjugate addition of alkyl phosphinates to Michael acceptors is an important method but requires substitution with an electron-withdrawing group;[9] therefore, addition to unactivated unsaturated hydrocarbons is considerably more difficult and typically uses a transition metal catalyst[3] or a free radical initiator.[4]



(1)

In 2005, we disclosed the inexpensive and straightforward nickel chloride-catalyzed addition of phosphinates to terminal and internal alkynes (eq 1).[10] In this reaction, $ROP(O)H_2$ plays several roles as a (a) reagent, (b) reducing agent to activate the nickel precatalyst, (c) ligand to stabilize the Ni(0) catalyst, and (d) drying agent when $NiCl_2$-hydrate or moisture is present.[10] Unfortunately, hydrophosphinylation of alkenes under similar conditions was not very successful (^{31}P NMR yield <70%), and at least not competitive with our palladium-catalyzed version.[10] Still, a nickel-catalyzed version of alkene hydrophosphinylation would be useful. Often in nickel catalysis, $Ni(cod)_2$ is the precursor, but it is an expensive (as costly as standard palladium salts) and highly air-sensitive species (requiring glovebox and related stringent inert-atmosphere techniques). On the other hand, nickel chloride is cheaper than palladium salts and its complexes by 2 orders of magnitude or more. Herein, we report our progress with this reaction and the successful addition of phosphinates to unactivated alkenes catalyzed by nickel chloride, in the presence of an external phosphine ligand.

RESULTS AND DISCUSSION

Although our early work indicated that phosphinates did add to olefins under nickel catalysis,[10] the yields were not satisfactory. Prompted by the preliminary results and our work with alkynes, we have investigated this nickel-catalyzed hydrophosphinylation reaction in more details and are now reporting a successful methodology to synthesize *H*-phosphinates through phosphinate addition to alkenes.

1-Octene was chosen as a representative example of an unactivated olefin. Ethyl phosphinate was prepared via our alkoxysilane method and used as a 0.5 M stock solution.[11a] Various conditions and catalysts were investigated as shown in Table 1.

As previously reported,[10] $NiCl_2$ alone does not work well with 1-octene (entry 1), but under similar conditions $Cl_2Ni(PPh_3)_2$ is more successful (entry 5), whereas heating in

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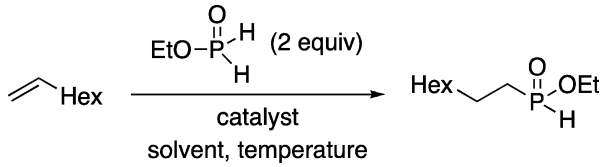
Table 1. Nickel Catalysis in the Hydrophosphinylation of 1-Octene with $EtOP(O)H_2$



entry	solvent	catalyst	^{31}P NMR yield (%)[a]
1	$PhCH_3$, rt	$NiCl_2$ (3 mol %)	25
2	CH_3CN, reflux	$Cl_2Ni(PPh_3)_2$ (4 mol %)	30
3	THF, reflux	$Cl_2Ni(PPh_3)_2$ (5 mol %)	47
4	$PhCH_3$, reflux	$Cl_2Ni(PPh_3)_2$ (4 mol %)	45
5	$PhCH_3$, rt	$Cl_2Ni(PPh_3)_2$ (4 mol %)	65
6	$PhCH_3$, rt	$NiCl_2$ (5 mol %) PPh_3 (20 mol %)	61
7	$PhCH_3$, rt	$Ni(PPh_3)_4$ (3 mol %)	0
8	$PhCH_3$, reflux	Cl_2Ni(dppp) (4 mol %)	20
9	$PhCH_3$, rt	Cl_2Ni(dppp) (4 mol %)	69
10	$PhCH_3$, rt	Cl_2Ni(dppe) (5 mol %)	96
11	$PhCH_3$, rt	$NiCl_2$ (3 mol %) dppe (3.3 mol %)	87
12	$PhCH_3$, rt	$NiCl_2$ (3 mol %) dppe (5 mol %)	93

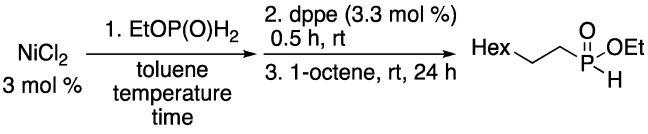
[a]NMR yields are determined by integration of all the resonances in the ^{31}P NMR spectra.

various solvents gives poorer results (entries 2–4). Addition of triphenylphosphine to $NiCl_2$ gives roughly similar results (entry 6), but the use of preformed $Ni(PPh_3)_4$ does not give any addition product (entry 7). As before, the reaction at room temperature is superior (entry 9 versus 8), but dppp (1, 3-bis(diphenylphosphino)propane) does not result in a very significant improvement over PPh_3. On the other hand, dppe (1, 2-bis(diphenylphosphino)ethane) gives much improved results (entries 10–12). Analysis of the reaction mixtures by gas chromatography usually indicated the complete disappearance of 1-octene with concomitant formation of octane and octene isomers, especially pronounced at higher temperatures.

Expectedly, this indicated that transfer hydrogenation[12] is one of the significant competing pathways. Because alkynes are more reactive than alkenes, competing pathways in hydrophosphinylation are less of a problem, and plain $NiCl_2$ is successful.[10] The results in Table 1 also allowed us to draw a few working hypotheses: (a) toluene is a good solvent, and room temperature is a requirement to maximize the yields; (b) the presence of a ligand has a significant influence on alkene hydrophosphinylation, and dppe appears to be the best choice. Fortunately, dppe is also the cheapest of the bidentate phosphine ligand family. Furthermore, on the basis of our prior work with alkynes and the identification of a preactivation process,[10] we knew that the reaction of $NiCl_2$ with an alkyl phosphinate[11] (at room temperature or with heating) results in the formation of a nickel(0) species corresponding to $Ni[(RO)P(OH)H]_4$ (^{31}P NMR δ ~170 ppm (d, J_{P-H} = 341 Hz)) in the absence of other ligands. This is not surprising since the reduction of nickel salts with phosphinates is the basis of the electroless plating process (Kanigen process), which is responsible for the major industrial consumption of phosphinates.[13]

A different experimental protocol was therefore investigated in which a nickel catalyst precursor is first prereacted with the phosphinate at room temperature for 2 h, *before* the addition of 1-octene, with or without dppe as an external ligand. Results are summarized in Table 2.

Table 2. Optimization of the Hydrophosphinylation of 1-Octene with $EtOP(O)H_2$ through Preactivation



entry	time	temp	^{31}P NMR yield (%)[a]
1	2 h	rt	100
2[b]	2 h	rt	61
3[c]	2 h	rt	57
4[d]	2 h	rt	98
5	8 h	rt	87
6	30 min	rt	59
7	2 h	85 °C	24
8	10 min	reflux	89

[a]NMR yields are determined by integration of all the resonances in the ^{31}P NMR spectra. [b]Without dppe. [c]Under air. [d]Cl_2Ni(dppe) was used.

This protocol results in clear improvements over the conditions of Table 1. Even $NiCl_2$ gives an almost 3-fold increase, even though it remains a moderate yield (entry 2). Preactivation of $NiCl_2$ at room temperature for 2 h before the addition of dppe was ideal (entry 1), and the process gives comparable results when preformed Cl_2Ni(dppe) is used (entry 4).

Not surprisingly, when oxygen is present, the yield drops significantly (entry 3). Longer preactivation at room temperature resulted in a small drop in yield (entry 5), but a larger one at the shorter 30 min time interval (entry 6). Consistent with Ni(0) decomposition, this was worse when heating was applied (entry 7); however, a short period of heating gave good results (entry 8). Preactivation was also tried with other nickel catalysts and ligands but failed to give better results.[14]

Scheme 1 shows possible mechanistic pathways for the reduction of the nickel(II) precursor into catalytically active Ni(0). Some alcohol (ROH) is typically present as a result of phosphinate synthesis.[11] The formation of *H*-phosphonates is always observed in the process. It should be noted that the hydrophosphonylation of alkenes that could result from their presence is not observed, even though various hydrophosphonylation processes have been described in the literature.[2,7]

Only alkyl phosphinates ($ROP(O)H_2$)[11] gave good results in this reaction, as was the case with alkynes. Hypophosphorous acid or its salts did not provide any significant yield of hydrophosphinylation (results not shown). This might be due to either increased transfer hydrogenation or less efficient formation of a nickel(0) species, the former being most likely.[15]

A plausible mechanism for the nickel-catalyzed hydrophosphinylation reaction is shown in Scheme 2. Complexation of nickel(0) to the P(III) phosphinate tautomer gives an intermediate, which can either decompose to a complexed dihydride leading to transfer hydrogenation,[12] or a monohydride that can add to unsaturated hydrocarbons.

The role of the ancillary ligand (for example, dppe) would be to stabilize the Ni(0) species and prevent/slow down the formation of the dihydride through β-hydrogen elimination leading to transfer hydrogenation. When alkynes are employed, a faster reaction rate allows hydrophosphinylation to take place under "ligandless" conditions.

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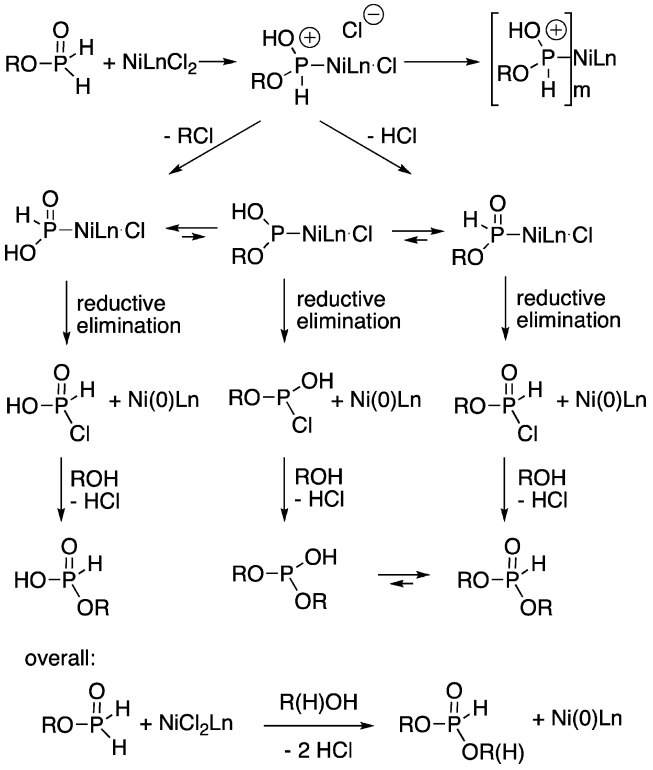
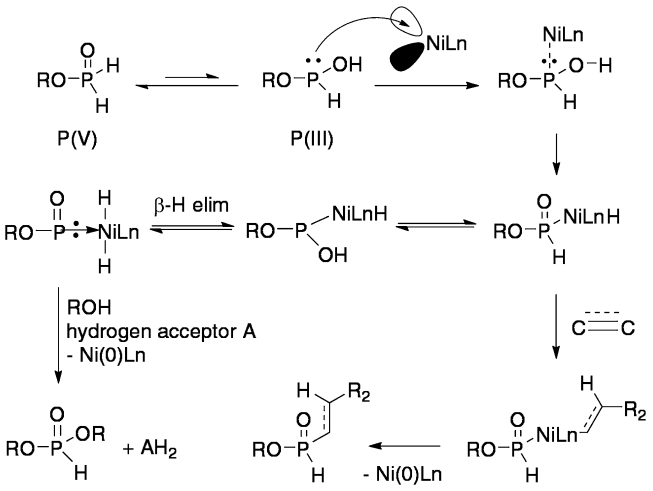
Scheme 1. Mechanistic Pathways in the Formation of Nickel(0) from Nickel(II) Species Using Alkyl Phosphinates



Scheme 2. Possible Mechanism for the Nickel-Catalyzed Hydrophosphinylation Reaction



With the above results in hand, a study of reaction scope was the logical next step. Thus, various terminal alkenes were explored as hydrophosphinylation substrates. Scheme 3 summarizes the results.

Ethyl phosphinate was prepared using (diethoxy)dimethyl silane and butyl phosphinate either through the analogous alkoxysilane method, or the Dean–Stark esterification of H_3PO_2, as reported previously.[11] Reactions following the conditions of Table 2 (entry 1) were then applied. Consistently high NMR yields were observed; however, isolated yields varied significantly, in large part because of the hydrolytic sensitivity of *H*-phosphinate esters during purification on silica gel.[10] Nonetheless, the present nickel-catalyzed alkene hydrophosphinylation reaction generally proceeded satisfactorily in yields often similar to our previously reported palladium-catalyzed methodology.[3c] For example, hydrophosphinylation of 1-octene was conducted on a 20 g scale, and the product was obtained in 79% yield, *without any chromatography*. However, some substrates such as allyl chloride, styrene, and 1*H*,1*H*,2*H*-perfluoro-1-octene failed (<40% NMR yield). Significant differences between Pd- and Ni-catalyzed reactions of phosphinates have been noticed previously.[16]

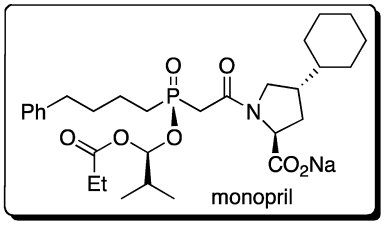
Later on it was discovered that the nickel catalyst also lowers the isolated yield through oxidation of the *H*-phosphinate product into the corresponding phosphonate monoester $R^1P(O)(OR)(OH)$. At this point, it was found that an extractive workup using dimethylglyoxime (a known nickel complexant) prior to purification helped improved the isolated yield.

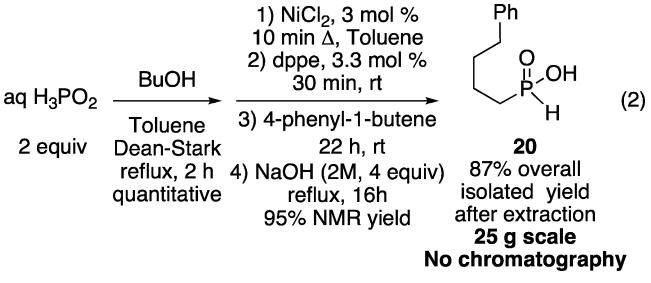
The potential for the desymmetrization of $ROP(O)H_2$ using a chiral phosphine ligand was briefly investigated (Table 3). Although a number of other chiral ligands were screened, results were unsatisfactory because the P–C bond-forming step gave low or no yield. As expected, dppe-like ligands provided good reactivity (entries 1 and 2). One josiphos-type ligand displayed good reactivity, while others simply did not give any hydrophosphinylation.

The highest enantiomeric excess observed was mediocre (18% de), but this was expected on the basis of our prior work with palladium-catalysts.[17] Perhaps a detailed screening might result in improved enantiomeric excesses, but this was not pursued further at this point, as we have already reported on the difficulties associated with the desymmetrization of phosphinates $ROP(O)H_2$.[17]

Because of the occasional discrepancies between NMR yields and isolated yields in Scheme 3, a different protocol was investigated next for the synthesis of more stable *H*-phosphinic acids. The idea was to prepare *H*-phosphinic acids through saponification of the crude hydrophosphinylation mixture, and purification through simple acidification/extraction. The results of this study are summarized in Table 4.

As expected, this process not only allows for increased isolated yields, but also avoids chromatographic purification altogether. On the basis of the conditions shown in Scheme 4, our nickel-catalyzed hydrophosphinylation/hydrolysis sequence was investigated with 4-phenyl-1-butene as the substrate (eq 2). Monopril (fosinopril) is a (pro)drug used in the treatment of congestive heart failure (angiotensin converting enzyme (ACE) inhibitor).[18] Its current synthesis involves the AIBN-initiated free radical hydrophosphinylation of 4-phenyl-1-butene with H_3PO_2, but a few percents of





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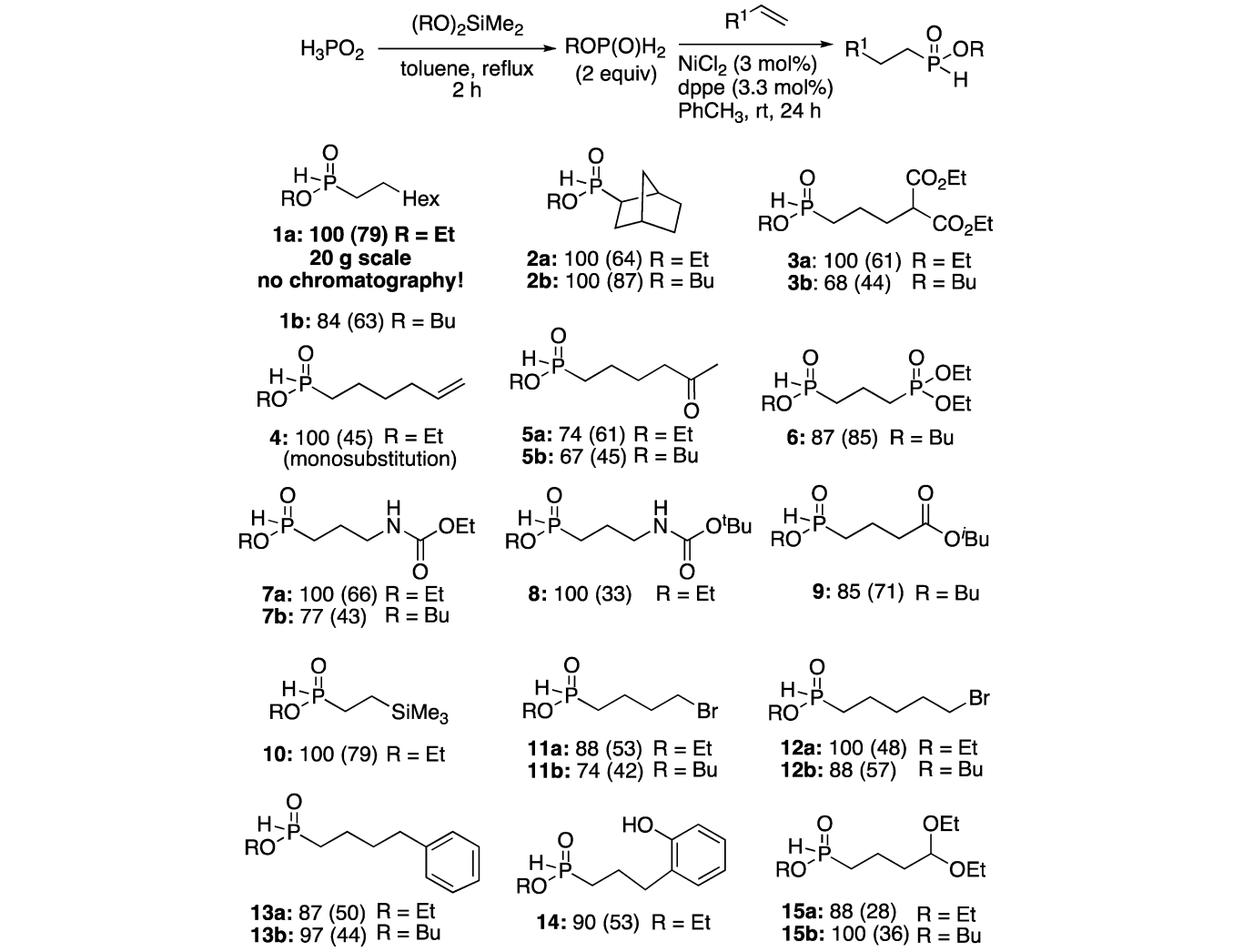
Scheme 3. Preliminary Scope of the Nickel-Catalyzed Hydrophosphinylation Reaction[a]

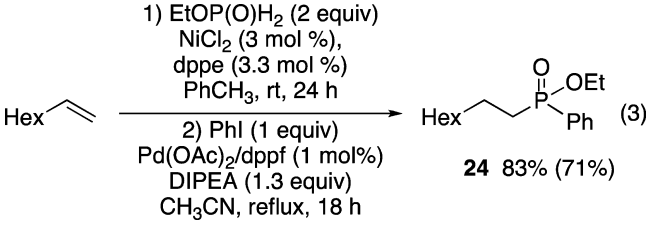


[a]^{31}P NMR yield (isolated yield).

a regioisomeric impurity (formation of the branched isomer) complicate the manufacture.[18a] With the nickel-catalyzed reaction, excellent yield of product was obtained with little or no formation of regioisomer (<0.5% as determined by ^{31}P NMR) on a relatively large laboratory scale, and again without any chromatography.

On the basis of the same idea, the conversion of crude *H*-phosphinate esters into other important organophosphorus compounds was examined next. Scheme 4 summarizes these results.

Another one-pot process of interest is the cross-coupling of the intermediate *H*-phosphinate (eq 3). Various literature conditions related to the cross-coupling of *H*-phosphinate with aryl halides have been reported.[19] However, in eq 3, standard conditions were employed since reactive iodobenzene was the coupling partner.[10]



Additionally, the present nickel-catalyzed hydrophosphinylation of alkenes can be employed instead of our palladium version in order to prepare various compounds more cheaply. Scheme 5 shows three such examples and their application to the synthesis of *P*-heterocycles.

Hydrophosphinylation of 5-bromo-1-pentene gives the desired addition product contaminated with $(EtO)_2P(O)H$, which was removed in vacuo. Addition of LiHMDS[20] to the resulting crude mixture formed the corresponding 1-ethoxyphosphorinane 1-oxide heterocycle in good isolated yield. Addition of ethyl phosphinate to allyl carbamate followed by acid hydrolysis gives the intermediate *H*-phosphinic acid in excellent yield (actually higher than with our palladium-catalyzed methodology).[21] Heterocyclization using the Kabachnick–Fields protocol[21,22] gave the corresponding *P*,*N*-heterocycle uneventfully, as we reported previously. Finally, hydrophosphinylation of the terminal alkene of methyl (*E*)-3-methyl-2,6-heptadienoate,[23] followed by cyclization through conjugate addition, delivered the substituted phosphorinanic ester.

■ CONCLUSION

The nickel-catalyzed hydrophosphinylation of terminal alkenes with alkyl phosphinates is described, using inexpensive nickel

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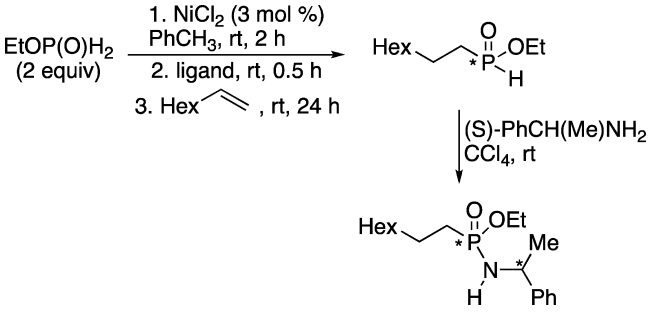
Table 3. Desymmetrization of $EtOP(O)H_2$ through Hydrophosphinylation Using a Chiral Ligand

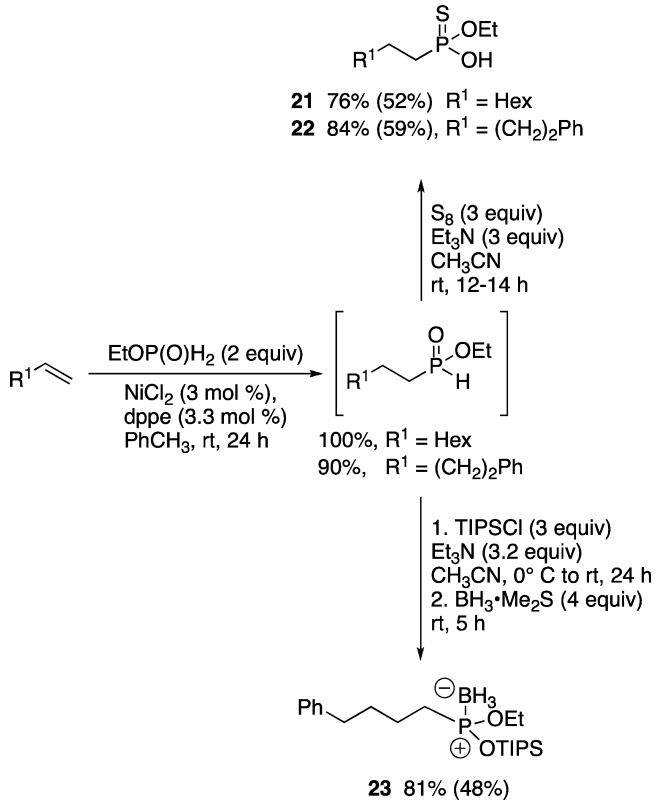


entry	ligand[a]	^{31}P NMR yield (%)[b]	de (%)[c]
1	(*R*,*R*)-DIPAMP	90	12
2	(*S*,*S*)-Chiraphos	89	18
3	(*S*,*S*)-Ph-BPE	69	16
4	JosiPhos-(*R*)-(*S*)-PDF-Pxyl$_2$	96	17
5	JosiPhos-(*R*)-(*S*)-PPFPCy$_2$	0	–
6	(*S*,*S*)-DIOP	0	–

[a]3.3 mol %. [b]NMR yields are determined by integration of all the resonances in the ^{31}P NMR spectra. [c]ee determination was conducted as in ref 17 using (*S*)-methyl-benzylamine and CCl_4.

chloride and dppe as the ancillary ligand. Experiments relevant to both synthetic and mechanistic aspects are described. A mechanism for the phosphinate reduction of nickel chloride into nickel(0) is provided and is relevant to the Kanigen electroless plating process. Similarly, a mechanism for the nickel-catalyzed hydrophosphinylation reaction is proposed, consistent with the data, and which rationalizes reactivity differences between alkenes and alkynes. Not only the method provides a cheap and practical alternative to our palladium-based methodology, it also provides a simple method for the catalyzed formation of phosphorus−carbon bonds from hypophosphorous derivatives. Indeed, in most cases the reaction is a one-pot process, and chromatographic purification can be completely avoided in many cases. The work is important as it establishes another dimension to the chemistry of phosphinates and is competitive with the traditional use of phosphorus trichloride in the synthesis of organophosphorus compounds. The conversion of phosphinates to *H*-phosphinates and other intermediates is indeed an important goal because it alleviates the need for toxic intermediates like elemental phosphorus (P_4), phosphine (PH_3), red phosphorus, and of course phosphorus trichloride. Our method could have industrial potential and provides a new link in the quest for environmentally more benign organophosphorus chemistry.

Scheme 4. Nickel-Catalyzed Hydrophosphinylation/Complexation Sequence[a]

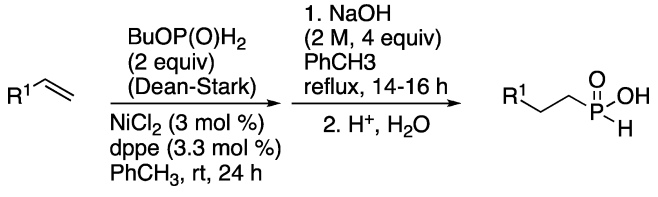


[a]^{31}P NMR yield (isolated yield).

EXPERIMENTAL SECTION

General Chemistry. All starting materials were purchased from commercial sources and used as received. The solvents were distilled under N_2 and dried according to standard procedures (toluene and acetonitrile from CaH_2; THF from Na/benzophenone ketyl; *N*,*N*-diisopropylethylamine was distilled from CaH_2 and stored over 4 Å

Table 4. Nickel-Catalyzed Hydrophosphinylation/Hydrolysis



Compound	Alkene	^{31}P NMR yield	Isolated yield (no chromatography)
16	Hex	(90 %)	82 % (7 g scale)
17	Oct	(93 %)	70 %
18		(100 %)	87 %
19		(100 %)	81 %

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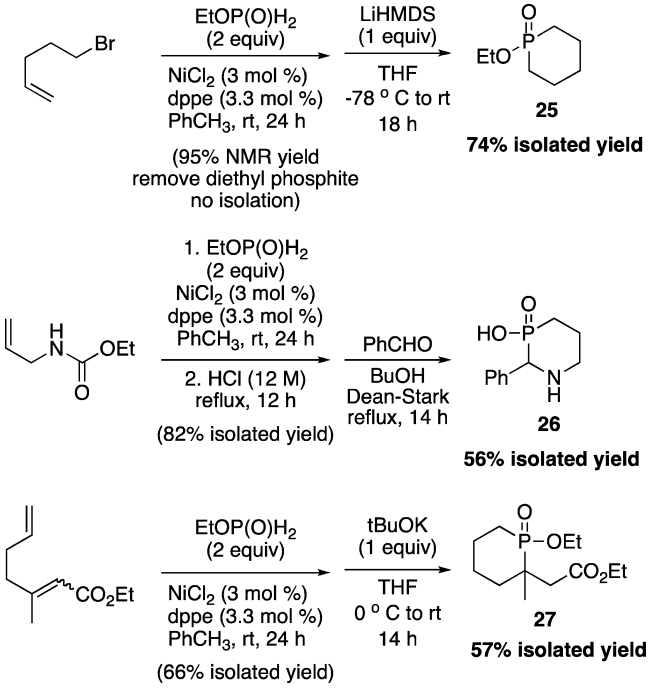
Scheme 5. Nickel-Catalyzed Hydrophosphinylation Applied to the Preparation of *P*-Heterocycles



molecular sieves). TLC analyses were performed on sheets precoated with silica gel $60F_{254}$. Compound detection was achieved by exposure to UV light (254 nm), by immersion in anisaldehyde stain (by volume: 93% ethanol, 3.5% H_2SO_4, 1% AcOH and 2.5% anisaldehyde) followed by heating at 150 °C. Flash chromatography experiments were carried out on Silica Gel premium Rf grade (40–75 μm). Ethyl acetate/hexane mixtures were used as the eluent for chromatographic purifications. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts for ^{1}H NMR are given in ppm relative to internal tetramethylsilane (δ = 0 ppm), using $CDCl_3$ as solvent. Chemical shifts for ^{13}C NMR are given in ppm relative to $CDCl_3$ (δ = 77.0 ppm). Chemical shifts for ^{31}P NMR spectra are given relative to external 85% phosphoric acid (δ = 0 ppm). Abbreviations used for signal patterns are as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet. High resolution mass spectra (HRMS) were obtained either by direct probe (EI/CI) and analyzed by magnetic sector, or by electrospray using a TOF analyzer.

^{31}P NMR Yield Measurements. The NMR yields are determined by integration of all the resonances in the ^{31}P spectra, an approach that is valid if no phosphorus-containing gas (i.e., PH_3) evolves, or if the precipitate in a heterogeneous mixture does not contain phosphorus. The yields determined by NMR are generally accurate within ~10% of the value indicated, and are reproducible. Isolated yields are sometimes significantly lower in the case of *H*-phosphinate esters because these are polar compounds and hydrolytically labile. This does not reflect an inaccuracy in the NMR yield, but instead the fact that *H*-phosphinates can be difficult to purify. Validation of NMR yields was conducted in ref 10.

Preparation of AlkOP(O)H_2 Stock Solution Using Alkoxysilanes. The preparation of these compounds was conducted as described in the literature.[11a] In a typical procedure, a solution of the preconcentrated H_3PO_2 (125 mmol), alkoxysilane (125 mmol for $(RO)_4Si$, or 250 mmol for $(RO)_2SiMe_2$, in reagent grade toluene (to 0.5 M concentration) is refluxed for 2 h under N_2. After cooling to room temperature, the solution was bottled and sealed with a septum, and the headspace was flushed with N_2. The solution was used for the subsequent hydrophosphinylation reactions directly without further purification.

Formation of AlkOP(O)H_2 with Alcohol Using Azeotropic Removal of Water. Augmented procedure previously reported in the literature.[4a] A flask containing preconcentrated H_3PO_2 (75 mmol) and alcohol (375 mmol) in reagent grade $PhCH_3$ (0.5 M) was equipped with a Dean–Stark trap prefilled with $PhCH_3$ and fitted with a condenser. The solution was refluxed under N_2 for 3 h and then cooled to room temperature. The solution was bottled and sealed with a septum, and the headspace was flushed with N_2. The solution was used for the subsequent hydrophosphinylation reactions directly without further purification.

General Procedure for the Preparation of Alkyl *H*-Phosphinates Using $NiCl_2$/dppe (Scheme 3). In an oven-dried 25 mL round-bottomed flask, $NiCl_2$ (0.075 mmol, 3 mol %) was suspended in 10 mL of a $ROP(O)H_2$ solution in $PhCH_3$ (0.5 M, 5 mmol, 2 equiv). The mixture was stirred at rt for 2 h, and dppe (0.0825 mmol, 3.3 mol %) was added. After 30 min, the alkene (2.5 mmol, 1 equiv) was added and the mixture was stirred at rt for 24 h. The solution was then washed with H_2O (10 mL × 2), sat. $NaHCO_3$ (10 mL), and brine (10 mL). Drying over $MgSO_4$ followed by rapid column chromatography on silica gel using EtOAc/Hexane mixtures afforded the corresponding *H*-phosphinate. The *H*-phosphinate compounds should be stored in CH_2Cl_2 solution (at least 0.5M) at 0 °C until ready to use.

Ethyl octylphosphinate (Scheme 3, 1a).[4b] Colorless oil, 20.638 g (79%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.01 (d, 1H, J = 526 Hz), 4.15–3.95 (m, 2H), 1.69 (m, 2H), 1.64 (m, 2H), 1.28 (t, 3H, J = 7.0 Hz), 1.19 (m, 10H), 0.80 (t, 3H, J = 6.2 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 40.1 (d, J_{PH} = 526 Hz).

Butyl octylphosphinate (Scheme 3, 1b).[3c] Colorless oil, 0.369 g (63%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.08 (d, 1H, J = 527 Hz), 4.17–3.93 (m, 2H), 1.82–1.27 (m, 18H), 0.95 (t, 3H, J = 7.3 Hz), 0.88 (t, 3H, J = 6.7 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 40.8 (d, J_{PH} = 526 Hz).

Ethyl norbornylphosphinate (Scheme 3, 2a).[4b] Colorless oil, 0.301 g (64%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.95 and 6.88 (d, 1H, 2*R* and 2*S* isomers, J = 521 Hz), 4.21–3.02 (m, 2H), 2.60 (dd, 1H, J = 36.6 Hz and J = 8.2 Hz); 2.38 (s, 1H), 1.92–1.22 (m, 9H), 1.36 (t, 3H, J = 7.0 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 44.2 and 42.4 (d, 2*R* and 2*S* isomers, J_{PH} = 521 Hz).

Butyl norbornylphosphinate (Scheme 3, 2b). Colorless oil, 0.470 g (87%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.93 and 6.87 (d, 1H, 2*R* and 2*S* isomers, J = 522 and 521 Hz), 4.16–3.92 (m, 2H), 2.60 (dd, 1H, J = 34.9 Hz and J = 8.9 Hz); 2.38 (s, 1H), 1.88–1.21 (m, 13H), 0.95 (t, 3H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 66.0 (d, CH_2, J_{POC} = 7.7 Hz), 40.4 (d, CH, J_{PC} = 95 Hz), 37.2 (CH_2), 37.1 (d, CH, J_{PCCC} = 10.1 Hz), 36.1 (d, CH, J_{PCC} = 9.2 Hz), 32.5 (d, CH_2, J_{POCC} = 5.8 Hz), 31.4 (d, CH_2, J_{PCC} = 17.4 Hz), 30.1 (d, CH_2, J_{PCCC} = 21.7 Hz), 28.6, 18.8 (CH_2), 13.6 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 44.7 and 43.0 (d, 2*R* and 2*S* isomers, J_{PH} = 520 and 521 Hz); HRMS (EI^+) m/z calcd. for $C_{11}H_{21}O_2P$ ($[M]^+$) 216.1279, found 216.1276.

Ethyl 4-(diethylmaleonate)propylphosphinate (Scheme 3, 3a). Colorless oil, 0.449 g (61%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12 (d, 1H, J = 530 Hz), 4.20 (q, 4H, J = 7.0 Hz), 4.09 (m, 2H), 3.34 (t, 1H, J = 7.3 Hz), 1.99 (m, 2H), 1.81 (m, 2H), 1.65 (m, 2H), 1.36 (t, 3H, J = 7.0 Hz), 1.27 (t, 6H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 168.9, 168.8 (C), 62.4, 61.3 (3 CH_2), 51.3 (CH), 29.2 (d, CH_2, J_{PCC} = 17.0 Hz), 28.5 (d, CH_2, J_{PC} = 96.2 Hz), 18.7 (CH_2), 16.2, 14.0, 13.9 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 38.3 (d, J_{PH} = 530 Hz); HRMS (methane chem ion) m/z calcd. for $C_{12}H_{24}O_6P$ ($[M + H]^+$) 295.1311, found 295.1308.

Butyl 4-(diethylmaleonate)propylphosphinate (Scheme 3, 3b). Colorless oil, 0.355 g (44%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.09 (d, 1H, J = 530 Hz), 4.20 (q, 4H, J = 7.3 Hz), 4.15–3.96 (m, 2H), 3.34 (t, 1H, J = 7.3 Hz), 2.00 (m, 2H), 1.84–1.63 (m, 6H), 1.42 (m, 2H), 1.28 (t, 3H, J = 7.0 Hz), 0.95 (t, 6H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 169.1 (2 C), 66.4 (d, CH_2, J_{POC} = 6.9 Hz), 61.6 (2 CH_2), 51.5 (CH), 32.4 (d, CH_2, J_{POCC} = 6.0 Hz), 29.4 (d, CH_2, J_{PCC} = 17.0 Hz), 28.5 (d, CH_2, J_{PC} = 94.1 Hz), 18.9 (2 CH_2), 14.1, 13.6 (3 CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 38.8 (d, J_{PH} = 530 Hz); HRMS (ammonia chem ion) m/z calcd. for $C_{14}H_{28}O_6P$ ($[M + H]^+$) 323.1624, found 323.1620.

Ethyl hex-5-enyl-1-phosphinate (Scheme 3, 4).[4b] Colorless oil, 0.198 g (45%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62 (d, 1H, J = 540 Hz),

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5.40 (m, 2H), 5.05−4.95 (m, 1H), 4.26−4.03 (m, 2H), 2.07 (m, 2H), 1.81−1.51 (m, 6H), 1.456 (t, 3H, J = 6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.8 (d, J_{PH} = 525 Hz).

Ethyl (5-oxohexyl)phosphinate (Scheme 3, 5a). Colorless oil, 0.293 g (61%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.11 (d, 1H, J = 529 Hz), 4.09 (m, 2H), 3.83 (m, 2H), 2.48 (t, 2H, J = 3 Hz), 2.15 (s, 3H), 1.83−1.59 (m, 4H), 1.36 (t, 3H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 207.8 (C), 62.1 (d, CH_2, J_{POC} = 6.5 Hz), 42.5 (CH_2), 29.6 (CH_3), 28.1 (d, CH_2, J_{PC} = 93 Hz), 23.9 (d, CH_2, J_{PCC} = 16 Hz), 19.9 (d, CH_2, J_{PCCC} = 2.7 Hz), 15.9 (d, CH_3, J_{POCC} = 6.04 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.2 (d, J_{PH} = 528 Hz). HRMS (EI$^+$) m/z calcd. for $C_8H_{17}O_3P$ ([M]$^+$) 192.0915, found 192.0922.

Butyl (5-oxohexyl)phosphinate (Scheme 3, 5b). Yellow oil, 0.248 g (45%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.10 (d, 1H, J = 529 Hz), 4.07 (m, 2H), 2.48 (t, 2H, J = 3 Hz), 2.16 (s, 3H), 1.73 (m, 8H), 1.43 (m, 2H), 0.95 (t, 3H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 208.1 (C), 66.1 (d, CH_2, J_{POC} = 7.09 Hz), 42.7 (CH_2), 32.2 (d, CH_2, J_{POCC} = 6.1 Hz), 29.8 (CH_3), 28.3 (d, CH_2, J_{PC} = 95 Hz), 24.1 (d, CH_2, J_{PCC} = 16 Hz), 20.1 (d, CH_2, J_{PCCC} = 2.7 Hz), 18.6 (CH_2), 13.3 (CH_3) ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.6 (d, J_{PH} = 529 Hz). HRMS (EI$^+$) calcd. for $C_{10}H_{21}O_3P$ ([M]$^+$) 220.1228, found 220.1224.

Diethyl 3-(butoxy-*H*-phosphinoyl)propylphosphonate (Scheme 3, 6). Yellow oil, 0.638 g (85%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12 (d, 1H, J = 531 Hz), 4.15−4.09 (m, 6H), 1.92 (m, 6H), 1.70 (m, 2H), 1.46 (m, 2H), 1.33 (t, 6H, J = 7.5 Hz), 0.95 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 66.3 (d, CH_2, J_{POC} = 6.9 Hz), 61.7 (d, 2 CH_2, J_{POC} = 6.5 Hz), 32.3 (d, CH_2, J_{POCC} = 6.04 Hz), 29.2 (dd, CH_2, $J_{P(H)C}$ = 93 Hz and $J_{P(OEt)2CCC}$ = 14.7 Hz), 26.2 (dd, CH_2, $J_{P(OEt)2C}$ = 141 Hz and $J_{P(H)CCC}$ = 15.1 Hz), 18.8 (CH_2), 16.4 (d, 2 CH_3, J_{POCC} = 6.04 Hz), 14.6 (d, CH_2, J_{PCC} = 2.04 Hz), 13.6 (CH_3) ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 37.3 (dd, J_{PH} = 532 Hz and $^4J_{P,P}$ = 4.0 Hz), 30.1 ($^4J_{P,P}$ = 4.0 Hz). HRMS (methane chem ion) calcd. for $C_{11}H_{27}O_5P_2$ ([M + H]$^+$) 301.1334, found 301.1340.

Ethyl 3-(*N*-ethylcarbamoyl)propylphosphinate (Scheme 3, 7a). Colorless oil, 0.368 g (66%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.13 (d, 1H, J = 533 Hz), 4.99 (m, 1H), 4.26−4.01 (m, 4H), 3.28 (m, 2H), 1.83 (m, 4H), 1.37 (t, 3H, J = 7.0 Hz), 1.24 (t, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 156.9 (C), 62.6 (d, CH_2, J_{POC} = 6.8 Hz), 60.7 (CH_2), 40.9 (d, CH_2, J_{PCCC} = 16.9 Hz), 26.0 (d, CH_2, J_{PC} = 94.6 Hz) 21.5 (CH_2), 16.3 (d, CH_2, J_{POCC} = 6.3 Hz), 14.7 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 38.9 (d, J_{PH} = 534 Hz); HRMS (methane chem ion) calcd. for $C_8H_{19}NO_4P$ ([M + H]$^+$) 224.1017, found 224.1014.

Butyl 3-(*N*-ethylcarbamoyl)propylphosphinate (Scheme 3, 7b). Colorless oil, 0.270 g (43%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.11 (d, 1H, J = 533 Hz), 5.60 (m, 1H), 4.10 (q, 2H, J = 6.2 Hz), 4.02 (m, 2H), 3.26 (m, 2H), 1.82 (m, 4H), 1.69 (m, 2H), 1.42 (m, 2H), 1.24 (t, 3H, J = 7.0 Hz), 0.95 (t, 3H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 157.1 (C), 66.4 (d, CH_2, J_{POC} = 6.8 Hz), 60.8 (CH_2), 41.0 (d, CH_2, J_{PCCC} = 15.9 Hz), 32.5 (d, CH_2, J_{POCC} = 6.3 Hz), 26.1 (d, CH_2, J_{PC} = 94.6 Hz), 21.7, 18.9 (CH_2), 14.8, 13.7 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.7 (d, J_{PH} = 533 Hz); HRMS (methane chem ion) calcd. for $C_{10}H_{23}NO_4P$ ([M + H]$^+$) 252.1365, found 252.1362.

Ethyl 3-(*N*-*tert*-butylcarbamoyl)propylphosphinate (Scheme 3, 8).[4b] Colorless oil, 0.210 g (33%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.11 (d, 1H, J = 534 Hz), 4.78 (br, 1H), 4.26−4.01 (m, 2H), 3.23 (m, 2H), 1.83 (m, 4H), 1.42, (s, 9H), 1.37 (t, 3H, J = 7.0 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.0 (d, J_{PH} = 532 Hz).

Isobutyl 4-(butoxy-*H*-phosphinoyl)butanoate (Scheme 3, 9). Colorless oil, 0.469 g (71%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.11 (d, 1H, J = 531 Hz), 4.12 (m, 2 H), 3.87 (d, 2H, J = 6.90 Hz), 2.46 (t, 2H J = 7.2 Hz), 1.92 (m, 4H), 1.69 (m, 2H), 1.41 (m, 2H), 0.93 (d, 6H, J = 6.7 Hz) ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 171.5 (C), 69.7 (CH_2), 65.3 (d, CH_2, J_{POC} = 7.2 Hz), 33.3 (d, CH_2, J_{PCCC} = 15.5 Hz), 31.4 (d, CH_2, J_{POCC} = 6.04 Hz), 26.9 (d, CH_2, J_{PC} = 93.9 Hz), 26.6 (CH), 18.0 (2 CH_3), 17.7 (CH_2), 15.4 (d, CH_2, J_{PCC} = 2.26 Hz), 12.6 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.0 (d, J_{PH} = 531 Hz) HRMS (ammonia chem ion) calcd. for $C_{12}H_{26}O_4P$ ([M + H]$^+$) 265.1569, found 265.1566.

Ethyl 2-(trimethylsilyl)ethylphosphinate (Scheme 3, 10). Colorless oil, 0.383 g (79%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.02 (d, 1H, J = 526 Hz), 4.23− 4.04 (m, 2H), 1.68 (m, 2H), 1.37 (t, 3H, J = 7.0 Hz), 0.71 (m, 2H), 0.00 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 64.4 (d, CH_2, J_{POC} = 6.9 Hz), 25.0 (d, CH_2, J_{PC} = 91.6 Hz), 18.5 (d, CH_3, J_{POCC} = 5.8 Hz), 8.3 (d, CH_2, J_{PCC} = 6.9 Hz), 0.00 (3 CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 43.5 (d, J_{PH} = 525 Hz); HRMS (ESI) calcd. for $C_7H_{20}O_2PSi$ ([M + H]$^+$) 195.0970, found 195.0963.

Ethyl 4-bromobutylphosphinate (Scheme 3, 11a).[24] Colorless oil, 0.303 g (53%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.13 (d, 1H, J = 530 Hz), 4.24−4.04 (m, 2H), 3.43 (t, 2H, J = 6.5 Hz), 1.99 (m, 2H), 1.80 (m, 4H), 1.38 (t, 3H, J = 7.0 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 38.8 (d, J_{PH} = 532 Hz).

Butyl 4-bromobutylphosphinate (Scheme 3, 11b). Colorless oil, 0.270 g (42%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12 (d, 1H, J = 530 Hz), 4.19−3.95 (m, 2H), 3.42 (t, 2H, J = 6.5 Hz), 2.00−1.60 (m, 8H), 1.41 (m, 2H), 0.95 (t, 3H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 66.4 (d, CH_2, J_{POC} = 6.8 Hz), 33.0 (d, CH_2, J_{PCCC} = 15.5 Hz), 32.8 (CH_2), 32.5 (d, CH_2, J_{POCC} = 5.8 Hz), 27.9 (d, CH_2, J_{PC} = 93.2 Hz), 19.6, 18.9 (CH_2), 13.7 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.1 (d, J_{PH} = 529 Hz); HRMS (methane chem ion) calcd. for $C_8H_{19}BrO_2P$ ([M + H]$^+$) 257.0306, found 257.0305.

Ethyl 5-bromopentylphosphinate (Scheme 3, 12a).[3] Colorless oil, 0.292 g (48%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.14 (d, 1H, J = 528 Hz), 4.26−4.01 (m, 2H), 3.42 (t, 2H, J = 6.5 Hz), 1.93−1.75 (m, 4H), 1.72−1.53 (m, 4H), 1.37 (t, 3H, J = 7.0 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.9 (d, J_{PH} = 522 Hz).

Butyl 5-bromopentylphosphinate (Scheme 3, 12b). Colorless oil, 0.386 g (57%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.14 (d, J = 525 Hz, 1H), 4.20−3.95 (m, 2H), 3.42 (t, J = 6.5 Hz, 2H), 1.93−1.53 (m, 12H), 1.37 (t, J = 7.0 Hz, 3H); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.9 (d, J_{PH} = 522 Hz).

Ethyl 4-phenylbutylphosphinate (Scheme 3, 13a).[25] Yellow oil, 0.283 g (50%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30−7.14 (m, 5H), 7.07 (d, 1H, J = 527 Hz), 4.20−3.98 (m, 2H), 2.63 (t, 2H, J = 7.3 Hz), 1.79−1.60 (m, 6H), 1.34 (t, 3H, J = 7.0 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.6 (d, J_{PH} = 527 Hz).

Butyl 4-phenylbutylphosphinate (Scheme 3, 13b).[25] Yellow oil, 0.280 g (44%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.37−7.18 (m, 5H), 7.14 (d, 1H, J = 527 Hz), 4.19−4.01 (m, 2H), 2.67 (t, 2H, J = 7.0 Hz), 1.89−1.65 (m, 8H), 1.43 (m, 2H), 0.97 (t, 3H, J = 7.3 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 40.2 (d, J_{PH} = 530 Hz).

Ethyl 3-(2-hydroxyphenyl)propylphosphinate (Scheme 3, 14). Light brown oil, 0.302 g (53%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39 (m, 1H), 7.12 (d, 1H, J = 535 Hz), 7.06 (m, 2H), 6.84 (m, 2H), 4.20−4.07 (m, 2H), 2.78 (t, 2H, J = 6.7 Hz), 2.05−1.74 (m, 4H), 1.36 (t, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 155.3 (C), 130.4, 127.7 (CH), 127.1 (C), 119.8, 115.8 (CH), 63.0 (d, CH_2, J_{POC} = 6.9 Hz), 30.7 (d, CH_2, J_{PCC} = 15.3 Hz), 27.9 (d, CH_2, J_{PC} = 95.3 Hz), 21.3 (d, CH_2, J_{PCCC} = 2.3 Hz), 16.4 (d, CH_3, J_{POCC} = 6.0 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 41.5 (d, J_{PH} = 534 Hz); HRMS (EI$^+$) calcd. for $C_{11}H_{17}O_3P$ ([M]$^+$) 228.0915, found 228.0916.

Ethyl 4,4-diethoxybutylphosphinate (Scheme 3, 15a). Yellow oil, 0.167 g (28%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.10 (d, 1H, J = 528 Hz), 4.48 (t, 1H, J = 4.7 Hz), 4.20−4.09 (m, 2H), 3.64 (m, 2H), 3.49 (m, 2H), 1.71 (m, 6H), 1.37 (t, 3H, J = 7.0 Hz), 1.21 (t, 6H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 102.5 (CH), 62.5 (d, CH_2, J_{POC} = 6.9 Hz), 61.1 (2 CH_2), 34.4 (d, CH_2, J_{PCCC} = 15.3 Hz), 28.7 (d, CH_2, J_{PC} = 93.6 Hz), 16.4 (d, CH_2, J_{PCC} = 2.9 Hz), 15.5 (3 CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.5 (d, J_{PH} = 528 Hz); HRMS (EI$^+$) calcd. for $C_{10}H_{23}O_4P$ ([M − H]$^+$) 237.1256, found 237.1257.

Butyl 4,4-diethoxybutylphosphinate (Scheme 3, 15b). Yellow oil, 0.240 g (36%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.08 (d, 1H, 526 Hz), 4.47 (m, 1H), 4.05 (m, 2H), 3.65−3.39 (m, 4H), 1.83−1.34 (m, 8H), 1.20 (t, 2H, J = 7.0 Hz) 0.93 (m, 9H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 102.5 (CH), 66.3 (d, CH_2, J_{POC} = 5.13 Hz), 65.7 (CH_2), 34.0 (d, CH_2, J_{PCCC} = 11.4 Hz), 32.4 (d, CH_2, J_{POCC} = 4.60 Hz), 28.8 (d, CH_2, J_{PC} = 93.9 Hz), 18.8 (CH_2),

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16.3 (CH_2), 15.3(CH_3), 13.6 (CH_3). HRMS (EI^+) calcd. for $C_{12}H_{27}O_4P$ ($[M - H]^+$) 265.1624, found 265.1621.

Representative Procedure for the Hydophosphinylation of Alkenes Followed by Hydrolysis (Table 4 and eq 2). In an oven-dried 25-mL round-bottom flask, anhydrous $NiCl_2$ (0.075 mmol, 3 mol %) is suspended in 10 mL of a $BuOP(O)H_2$ solution in $PhCH_3$ (0.5 M, 5 mmol, 2 equiv). The mixture is heated for 10 min until the nickel starts to dissolve, and the reaction mixture is cooled to room temperature (~15 min). Dppe (0.0825 mmol, 3.3 mol %) is added, and after 30 min of stirring, the alkene (2.5 mmol, 1 equiv) is added, and the mixture is stirred at room temperature for 24 h. Upon completion of the first reaction, aqueous NaOH solution (2 mL, 10 mmol, 4 equiv) is poured into the flask and refluxed for 12−14 h. The reaction mixture is first extracted with 10 mL of *t*-$PhCH_3$, acidified with 10 mL of saturated $NaHSO_4$ solution (pH < 2), and then extracted with 10 mL of EtOAc three times. The organic layer was dried over $MgSO_4$ and concentrated by rotary evaporation.

Octylphosphinic acid (Table 4, Entry 1, 16).[4a] Yellow oil, 5.699 g (82%): ^1H NMR ($CDCl_3$, 300 MHz) δ 11.55 (br, 1H), 7.11 (d, 1H, J = 541 Hz), 1.78 (m, 2H), 1.61 (m, 2H), 1.29 (m, 10 H), 0.90 (t, J = 4.4 Hz, 3H); ^{31}P NMR ($CDCl_3$ 121.47 MHz) δ 37.8 (d, J_{PH} = 540 Hz).

Decylphosphinic acid (Table 4, Entry 2, 17).[4a] Yellow oil, 0.361 g (70%): ^1H NMR ($CDCl_3$, 300 MHz) δ 8.81 (br, 1H), 7.05 (d, 1H, J = 537 Hz), 1.90−1.05 (m, 18H), 0.88 (t, 3H, J = 6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 38.1 (d, J_{PH} = 540 Hz).

Norbornylphosphinic acid (Table 4, Entry 3, 18). Yellow oil, 0.348 g (87%): ^1H NMR ($CDCl_3$, 300 MHz) δ 10.59 (br s, 1H), 6.95 (d, 1H, J = 536 Hz), 2.63 (m, 1H), 2.40 (m, 1H), 1.83−1.23 (m, 9H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 40.4 (d, CH, J_{PC} = 97 Hz), 37.4 (CH_2), 37.2, 36.3 (CH), 31.6 (d, CH_2, J_{PCC} = 16 Hz), 30.2, 28.7 (CH_2); ^{31}P NMR ($CDCl_3$ 121.47 MHz) δ 40.8 (d, J_{PH} = 531 Hz). HRMS (EI^+) calcd. for $C_7H_{13}O_2P$ ($[M]^+$) 160.0653, found 160.0654.

Hex-5-enyl-1-phosphinic acid (Table 4, Entry 4, 19).[4a] Yellow oil, 0.301 g (81%): ^1H NMR ($CDCl_3$, 300 MHz) δ 9.93 (br, 1H), 7.12 (d, 1H, J = 530 Hz), 5.60−5.20 (m, 3H), 2.07 (m, 2H), 1.65 (m, 6H); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 41.3 (d, J_{PH} = 530 Hz).

(4-Phenylbutyl)phosphinic acid (eq 2, 20).[4a] Yellow oil, 21.554 g (87%): ^1H NMR ($CDCl_3$, 300 MHz) δ 10.35 (br, 1H), 7.08 (d, 1H, J = 540 Hz), 7.25 (m, 5H), 2.64 (t, 2H, J = 7 Hz), 1.75 (m, 6H); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 38.0 (d, J_{PH} = 540 Hz).

Representative Procedure for the Hydrophosphinylation of Alkenes Followed by Formation of Phosphonothioic Acid *O*-Ethyl Ester (Scheme 4).[10] Nickel-catalyzed hydrophosphinylation of alkenes was conducted as described in the procedure for Scheme 3. The crude reaction mixture was washed once with deionized H_2O and concentrated under a vacuum at 50 °C to remove the residual diethyl phosphite. The crude reaction mixture was dissolved in 10 mL of freshly distilled CH_3CN. To this solution was added sulfur (0.24 g, 7.5 mmol, 3 equiv) and Et_3N (0.762 g, 7.53 mmol, 3 equiv) at room temperature. The resulting mixture was stirred at room temperature overnight. The solution was extracted with hexane, and the CH_3CN layer was partitioned between 1 M HCl and EtOAc. The organic layer was dried over $MgSO_4$ and concentrated to afford the crude compound. Purification over silica gel (Hexane to Hexane/EtOAc, 90/10 v/v) produced the expected compounds as brown oils.

***O*-Ethyl *O*-hydrogen octylphosphonothioate (21).** Brown oil, 0.309 g (52%): ^1H NMR ($CDCl_3$, 300 MHz) δ 418 (m, 2H), 2.01 (m, 2H), 1.66 (m, 2H), 1.36−1.27 (m, 14H), 0.88 (t, 3H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 61.9 (CH_2), 34.6 (d, CH_2, J_{PC} = 109 Hz), 31.7, 30.4, 30.3, 30.1, 29.0, 22.6 (CH_2), 16.1 (d, CH_3, J_{POCC} = 7.3 Hz), 14.0 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 94.6 (s); HRMS (EI^+) calcd. for $C_{10}H_{23}O_2PS$ ($[M]^+$) 238.1156, found 238.1152.

***O*-Ethyl *O*-hydrogen (4-phenylbutyl)phosphonothioate (22).** Brown oil, 0.381 g (59%): ^1H NMR ($CDCl_3$, 300 MHz) δ 7.31−7.14 (m, 5H), 4.22−4.09 (m, 2H), 2.65 (m, 2H), 2.06 (m, 2H), 1.74 (m, 4H), 1.31 (t, 3H, J = 10 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 140.9 (C), 127.3, 124.8 (5 CH), 60.8, 34.3, 32.7, 31.1, 21.4 (CH_2), 15.1 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 94.3 (s); HRMS (EI^+) calcd. for $C_{12}H_{19}O_2PS$ ($[M]^+$) 258.0843, found 258.0839.

Ethoxy(triisopropylsilyloxy)phenylbutylphosphine-borane (23).[26] TIPSCl (1.5 mL, 7 mmol, 1.4 equiv) was placed into a oven-dried round-bottom flask and cooled to 0 °C, under N_2. Et_3N (1 mL, 7.5 mmol, 1.5 equiv) was then added dropwise, and the reaction mixture was stirred for approximately 10 min at 0 °C. In a separate oven-dried round-bottom flask, a solution of crude ethyl 4-phenylbutylphosphinate (5 mmol, 1 equiv) in freshly distilled CH_3CN (10 mL) was cooled to 0 °C, under N_2. The mixture of TIPSCl/Et_3N was slowly added to the *H*-phosphinate solution via syringe, and the reaction mixture was maintained at 0 °C for 10−15 min, at which time the reaction was allowed to warm up to room temperature and stirred for 14 h under N_2. The reaction mixture was treated with $BH_3{\cdot}Me_2S$ (2.0 M in THF, 5 mL, 10 mmol, 2 equiv) by dropwise addition at room temperature. After 5 h, the reaction mixture was concentrated under reduced pressure, and the residue was partitioned between deionized H_2O and EtOAc. The aqueous layer was extracted with EtOAc (3×), and the combined organic layers were washed with brine (1×), dried over $MgSO_4$, and concentrated in vacuo to afford the crude compound. Purification by column chromatography over silica gel (Hexane/$PhCH_3$, 100:0 to 90:10, v/v) afforded 0.476 g (48%) of the desired product as a colorless oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.06 (d, 1H, J = 529 Hz), 7.3−7.1 (m, 5 H), 4.25−3.95 (m, 2 H), 2.63 (t, 2H, J = 7 Hz), 1.90−1.55 (m, 6 H), 1.34 (t, 3 H, J = 7 Hz), 1.06 (m, 21 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 141.9, 128.6, 126.1 (5 CH, 1 C), 62.5 (d, CH_2, J_{POC} = 7 Hz), 35.6 (CH_2), 32.4 (d, CH_2, J_{PCCC} = 15 Hz), 28.9 (d, CH_2, J_{PC} = 94 Hz), 20.6 (CH_2), 16.6 (6 CH_3), 16.5 (d, CH_3, J_{POCC} = 6 Hz), 11.6 (3 CH) ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 134.7 (q, J_{PB} = 48 Hz) HRMS (EI^+) calcd. for $C_{21}H_{42}BO_2PSi$ ($[M]^+$) 396.2785, found 396.2788.

Representative Example of Hydrophosphinylation Followed by Cross-Coupling (eq 3, 24).[20] Nickel-catalyzed hydrophosphinylation was conducted as described in the procedure for Scheme 3 using 1-octene as the alkene (2.5 mmol, 1 equiv). The crude reaction mixture was washed once with deionized H_2O and concentrated under a vacuum at 50 °C to remove the residual diethyl phosphite. To a solution of crude ethyl octylphosphinate (2.5 mmol, 1.0 equiv) in freshly distilled CH_3CN (10 mL), was added an iodobenzene (2.5 mmol, 1.0 equiv), DIPEA (5.2 mmol, 1.3 equiv), $Pd(OAc)_2$ (0.025 mmol, 1 mol %) and dppf (0.028 mmol, 1.1 mol %) at room temperature. The solution was heated for 24 h at reflux in CH_3CN, under N_2. After cooling to room temperature, the crude mixture was concentrated in vacuo, and the residue was partitioned between deionized H_2O and EtOAc, followed by extraction of the aqueous phase with EtOAc (3×). The organic fractions were combined and washed with brine (1×). Drying and concentration furnished the crude compound, which was purified by column chromatography using EtOAc/Hexane mixtures to obtain 0.501 g (71%) of compound 24 as a brown oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.78 (m, 2H), 7.49 (m, 3H), 4.13−3.85 (dm, 2H), 1.84 (m, 2H), 1.70 −1.22 (m, 15H), 0.85 (t, 3H, J = 6.1 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 44.9 (s).

1-Ethoxy-phosphinane-1-oxide (Scheme 5, 25).[27] Compound **12a**, ethyl 5-bromopentylphosphinate (5 mmol, 1 equiv), was prepared by the standard hydrodrophosphinylation procedure. The crude product was partioned between deionized H_2O and EtOAc to remove the formed diethyl phosphite. The dried and concentrated product was diluted with anhydrous THF (25 mL) under N_2. The flask was placed at −78 °C and deoxygenated under a vacuum for 5 min. The reaction flask was backfilled with N_2, and LHMDS (1.0 M in THF, 5 mL, 5 mmol, 1 equiv) was added at −78 °C. After 10 min, the temperature of the solution was slowly allowed to warm to rt. After 3 h at rt, the reaction mixture was quenched with NH_4Cl/brine, extracted with EtOAc (3×), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting oil was purified by column chromatography on silica gel using mixtures of EtOAc/Hexane to afford 0.603g (74%) of a yellow oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 4.06 (m, 2 H), 2.03−1.63 (m, 10H), 1.37 (t, 3H, J = 6.9 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 50.08 (s).

3-Hydroxy-2-phenyl-1,3-azaphosphorinane-3-oxide (Scheme 5, 26).[21] Compound **7a**, ethyl 3-(*N*-ethylcarbamoyl)propylphosphinate (10 mmol), was prepared by the standard hydrophosphinylation procedure.

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Upon completion, the reaction mixture was concentrated in vacuo to remove $PhCH_3$, and aq. HCl (12 N, 50 mL) was added to the flask. After 16 h of reflux, the mixture was concentrated under a high vacuum. The residue was diluted with H_2O and washed with EtOAc (3 × 20 mL). Concentration of the aqueous layer afforded 1.830 g (82%) of 3-aminopropyl-*H*-phosphinic acid hydrochloride as a yellow oil. Immediately following, the *H*-phosphinic acid was diluted in *n*-butanol (0.2 M), and 1 equiv of the benzaldehyde was added. The mixture was refluxed for 16 h. After cooling, the precipitate was filtered and washed with *n*-butanol and then with Et_2O and dried under a high vacuum to obtain 0.970 g (56%) of the expected compound as a white solid: ^{1}H NMR (D_2O, 300 MHz) δ 7.31 (m, 5H), 4.21 (d, 1H, J = 6.6 Hz), 3.42 (d, Jgem = 13 Hz, 1H equatorial), 3.05 (m, 1H axial), 2.20−2.06 (m, 2H), 1.74 (m, 2H); ^{31}P NMR (D_2O, 121.47 MHz) δ 23.4 (m).

Ethyl 2-(1-ethoxy-2-methyl-1-oxidophosphinanyl)acetate (Scheme 5, 27). An ethyl *H*-phosphinate was prepared from ethyl 3-methylhepta-2,6-dienoate using the standard nickel hydrophoshinylation procedure. Ethyl 7-(ethoxy-*H*-phosphinoyl)-3-methyl-2-heptenoate was obtained as a yellow oil in 66% isolated yield. To a solution of *H*-phosphinate in THF (0.08 M, 0.76 mmol) at 0 °C, was added *t*BuOK (0.76 mmol, 1 equiv). The solution was stirred for 1 h at 0 °C and rt for 16 h. The reaction mixture was neutralized with 1 N HCl and extracted with EtOAc (3× 10 mL). Initial analysis of the product showed significant cleavage of the ester group. The compound was diluted in CH_3CN and treated with EtOH (1.16 mmol, 1.5 equiv), EDC (1.16 mmol, 1.5 equiv) and DMAP (0.076 mmol, 10 mol %). After 2 h of stirring at rt, the solution was extracted with saturated $NaHSO_4$ (1 × 10 mL), 1 N $NaHCO_3$ (1 × 10 mL), and brine (1 × 10 mL). After drying with $MgSO_4$ and concentrating in vacuo, 0.116 g (57%) of a brown oil was obtained: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.19−4.08 (m, 4H); 2.65 (m, 2H); 2.05−1.43 (m, 8H); 1.35−1.25 (m, 9H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 171.1 (C), 60.6 (d, CH_2, J_{POC} = 8.68 Hz), 37.5 (C), 36.6 (d, CH_2, J_{PC} = 88 Hz), 35.3, 30.9 (CH_2), 24.1 (d, CH_2, J_{PCCC} = 3.40 Hz), 23.1, 21.2 (CH_2), 18.9 (CH_3), 16.9 (d, CH_3, J_{POCC} = 5.36 Hz), 14.1 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 53.3 (m); HRMS (EI^+) calcd. for $C_{12}H_{23}O_4P$ ($[M]^+$) 262.1334, found 262.1334.

■ ASSOCIATED CONTENT

Supporting Information

Tables S1 and S2 and copies of the NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: j.montchamp@tcu.edu.

Notes

The authors declare no competing financial interest.

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