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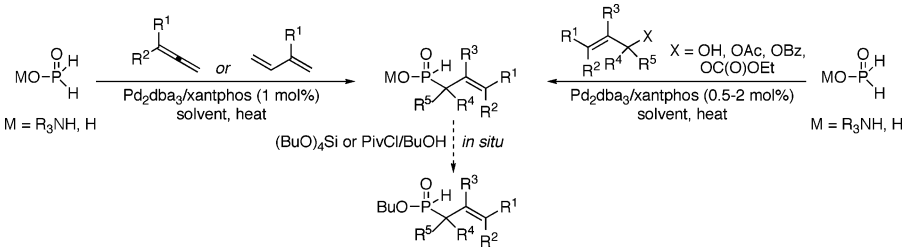
Palladium-Catalyzed Reactions of Hypophosphorous Compounds with Allenes, Dienes, and Allylic Electrophiles: Methodology for the Synthesis of Allylic *H*-Phosphinates

Karla Bravo-Altamirano, Isabelle Abrunhosa-Thomas, and Jean-Luc Montchamp*

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

j.montchamp@tcu.edu

Received November 27, 2007



Hypophosphorous compounds ($MOP(O)H_2$, M = H, R_3NH) effectively participate in metal-catalyzed C−P bond-forming reactions with allenes, dienes, and activated allylic electrophiles under mild conditions. The catalytic system Pd_2dba_3/xantphos is crucial to avoid or minimize the competitive reductive transfer-hydrogenation pathway available to hypophosphorous acid derivatives. Further investigation into the allylation mechanism provided access to the analogy *allylic acetate−allylic phosphinate*, which then led to the development of a Pd-catalyzed rearrangement of preformed allylic phosphinates esters and, ultimately, to a catalytic dehydrative allylation of hypophosphorous acid with allylic alcohols. The reactions disclosed herein constitute efficient synthetic approaches, not only to prepare allylic *H*-phosphinic acids but also their esters via one-pot tandem processes. In addition, the potential of *H*-phosphinates as useful synthons for the preparation of other organophosphorus compounds is demonstrated.

Introduction

Homogeneous catalysis has become a powerful methodology for constructing C−P bonds as a result of the advantages that it represents in terms of reactivity, selectivity and functional group tolerance.[1] In fact, metal-catalyzed P−H bond addition and cross-coupling reactions have already been the subject of some reviews[2] and constitute areas of significant current interest due to the increasing number of applications and better understanding of the biological role of organophosphorus compounds. Recent efforts have mainly been directed toward the development of catalytic methodologies for the preparation of phosphines, either by the direct functionalization of air-sensitive phosphines or through the intermediacy of phosphine oxides and phosphine−borane complexes.[3] In contrast, given the thermal instability and/or possibility for competitive transfer−hydrogenation[4] reactions that characterize hypophosphorous compounds **1** ($MOP(O)H_2$ M = H, R_3NH, Alk, Na, etc.), the metal-catalyzed functionalization of these compounds as a preparatively useful methodology to access *H*-phosphinic acid derivatives has been less studied. Nonetheless, our group effectively overcame the reductive pathway[4] and reported the first examples of Pd- and Ni-catalyzed addition reactions of hypophosphorous compounds to alkenes and alkynes leading to highly versatile *H*-phosphinate synthons.[5] With regard to Pd-catalyzed cross-coupling reactions, Schwabacher described the first examples of cross-coupling between alkyl phosphinates ($AlkOP(O)H_2$) and aryl iodides.[6] However, it was not until recently that we reported more general and convenient protocols for the coupling of hypophosphorous compounds with a wide range of aryl and alkenyl halides and triflates, as well as the first example of a Ni-

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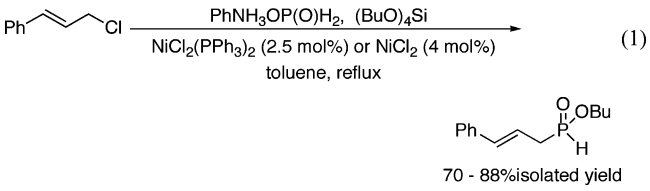
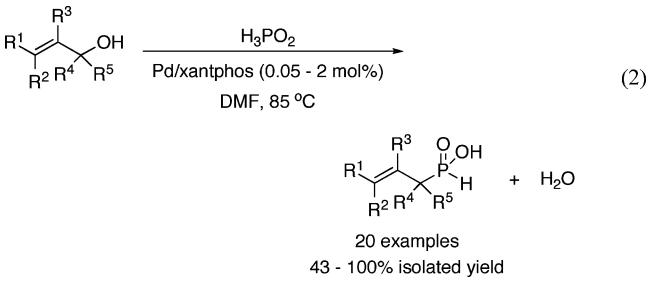
10.1021/jo702542a CCC: $40.75
Published on Web 02/15/2008

catalyzed cross-coupling of an alkyl phosphinate with an allylic halide (eq 1).[7] Recently, Zhao reported a single example of a Cu-cross-coupling between iodobenzene and ammonium hypophosphite.[8]



Although the allylic-*H*-phosphinates accessible through this route could be more conveniently prepared by the base-promoted alkylation with allylic halides,[9] subsequent studies led us to discover more efficient routes to prepare these compounds from readily available starting materials and, ultimately, allylic alcohol feedstocks (eq 2).[10] Herein, we not only unveil new reactivity patterns of hypophosphorous compounds with allylic electrophiles and unsaturated substrates, but we also report on useful Pd-catalytic methods to prepare allylic-*H*-phosphinic acids and *H*-phosphinate esters, such as hydrophosphinylation, allylation, rearrangement, and tandem allylation−esterification. The synthetic flexibility of *H*-phosphinates is also illustrated with the synthesis of *P*-heterocycles.



Results and Discussion

Reactivity of Allenes and Dienes in the Pd-Catalyzed Hydrophosphinylation Reaction. Our work began with an investigation of the reactivity of hypophosphorous acid (H_3PO_2−**1a**) and its anilinium salt ($PhNH_3OP(O)H_2$−**1b**) in the Pd-catalyzed addition to allenes and dienes (Tables 1 and 2). Pd_2dba_3/xantphos (1 mol %) was selected as the catalytic system based on our previous work with alkenes and alkynes.[5a] The reaction solvent proved also important: acetonitrile and DMF gave the best results in reactions performed with H_3PO_2, while DMF was required with amine salts of hypophosphorous acid. Isolation of the products consisted of a simple acidic extractive workup. Allenes were synthesized in moderate yields by homologation of acetylenes[11] or by Pd-catalyzed hydrogenolysis of alk-2-ynyl carbonates with ammonium formate[12] and then reacted in the Pd-catalyzed hydrophosphinylation reaction. As indicated in Table 1, a 3,3-disubstituted allene (entry 1) and the aromatic monosubstituted phenylallene (entry 2) reacted regioselectively and with high *E*-selectivity (>98:2 E/Z) to give allylic-*H*-phosphinic acids in good yields. On the other hand, the monosubstituted aliphatic cyclohexylallene reacted with low

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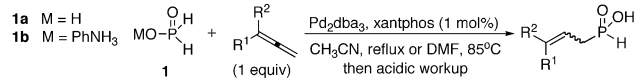
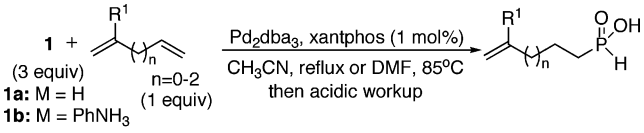
TABLE 1. Pd-Catalyzed Hydrophosphinylation of Allenes[a]



entry	1 (equiv)	allene R^1	allene R^2	solvent	product	% yield[b] (E/Z)[c]
1a	**1a** (2)	-$(CH_2)_5$-		CH_3CN	H_2O_2P	54
1b	**1b** (2)			DMF		64
2a	**1a** (2)	Ph	H	CH_3CN	H_2O_2P, Ph	100
2b	**1b** (2)			DMF		98
3	**1b** (2)	Cy	H	DMF	H_2O_2P, Cy	52 (95/5)

[a] Reactions were conducted with concentrated H_3PO_2. Solvents: reagent-grade CH_3CN or dry DMF (0.2 M). Reaction times: 8−14 h. Details can be found in the Experimental Section. [b] Isolated yield after extractive workup. [c] E/Z ratios were determined by ^1H NMR spectroscopy. Unless otherwise noted, E/Z > 98/2.

TABLE 2. Pd-Catalyzed Hydrophosphinylation of Dienes[a]



entry	1	substrate	solvent	product	% yield[b]
1	**1b**	R= Me	DMF	R, PO_2H_2	57
2	**1b**	R= Prenyl	DMF	R, PO_2H_2	59[c]
3	**1a**	$(CH_2)_2$	CH_3CN	H_2O_2P, $(CH_2)_4$	70

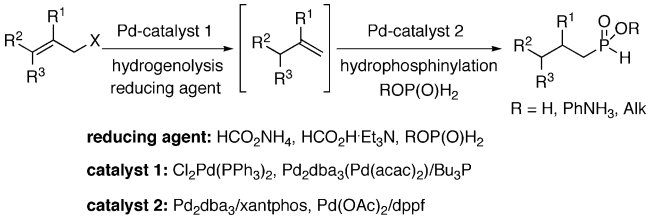
[a] Reactions were conducted with concentrated H_3PO_2. Solvents: reagent-grade CH_3CN or dry DMF (0.2 M). Reaction times: 8−14 h. Details can be found in the Experimental Section. [b] Isolated yield after extractive workup. [c] 1:1 mixture of isomers.

regio- and stereoselectivity with H_3PO_2. However, this stereoselectivity was significantly improved with anilinium hypophosphite **1b** (entry 3).

Several commercial dienes and enynes were also tested in the hydrophosphinylation reaction, and the results are summarized in Table 2. In general, conjugated dienes (i.e., 1,3-pentadiene) did not undergo addition with hypophosphorous compounds. However, isoprene or its derivatives (Table 2, entries 1 and 2) proved to be an exception to this behavior; this is probably due to the fact that rearrangement can take place, leading to the more stable allylic-*H*-phosphinic acid. Interestingly, with a nonconjugated diene (entry 3), the mono-*H*-phosphinic acid can be formed as a result from the selective addition of H_3PO_2 to one of the terminal double bonds, but no cyclization product was detected, supporting reversible hydropalladation (and not phosphinylpalladation) as we originally proposed. Enynes selectively reacted at the alkyne functionality; however, no significant regio- or stereoselectivity was observed, which resulted in intractable mixtures of isomers.

Related to the present research is the hydrophosphonylation of allenes with pinacol-*H*-phosphonate reported by Tanaka;[3ai] however, the synthetic flexibility of pinacol phosphonate esters

SCHEME 1. Tandem Hydrogenolysis−Hydrophosphinylation Process



is very limited compared to that of *H*-phosphinates.[13] However, even though some allenes and dienes selectively participate in the hydrophosphinylation reaction to afford allylic-*H*-phosphinic acids, the use of this methodology is rather limited and inconvenient from a practical point of view (limited availability of starting materials and/or poor selectivity). Nonetheless, the atom-economy offered by addition reactions is attractive and makes some of these transformations viable approaches to certain intermediates, such as isoprene-derived 3-methylbuten-2-ylphosphinic acid (Table 2, entry 1).

Pd-Catalyzed Allylation and Tandem Allylation−Esterification of Hypophosphorous Compounds with Activated Allylic Electrophiles. Even though the efficiency of metal-catalyzed allylic substitutions in constructing carbon−carbon and carbon−heteroatom bonds has been soundly demonstrated,[14] at the time we started our investigations, there were only two reports that described the use of this technique in the formation of C−P bonds (our group recently published another example; see eq 2). Fiaud developed the reaction of thiophosphides with allylic acetates using Pd catalysts,[15] while Lu et al. showed that dialkyl phosphites, diphenylphosphine oxide, and phenyl- or methyl-*H*-phosphinate esters react with allylic acetates or carbonates in presence of stoichiometric amounts of BSA (bis-(trimethylsilyl)acetamide) and the highly air-sensitive $Ni(cod)_2$ as catalyst.[16] Nevertheless, preliminary data from our group regarding the metal-catalyzed allylation of $AlkOP(O)H_2$ with allylic chlorides (eq 1)[7d] suggested the feasibility for a process of this kind to take place with non-halogenated and more widely available allylic alcohols derivatives, such as acetates or carbonates. Initially, we found that in presence of a Pd catalyst ($Pd(OAc)_2$/dppf), $AlkOP(O)H_2$ could react like formates, with hydrogenolysis of allylic chlorides to yield alkenes. The alkene could then undergo hydrophosphinylation.[7d] Then, we surmised that the optimum catalyst combination could lead to a tandem hydrogenolysis−hydrophosphinylation reaction of acetates with hypophosphorous compounds (Scheme 1). Surprisingly, when using a mixture of $PdCl_2(PPh_3)_2$ (for reduction) and Pd_2dba_3/xantphos (for hydrophosphinylation) in the reaction of cinnamyl acetate with anilinium hypophosphite **1b** in DMF (85 °C), a

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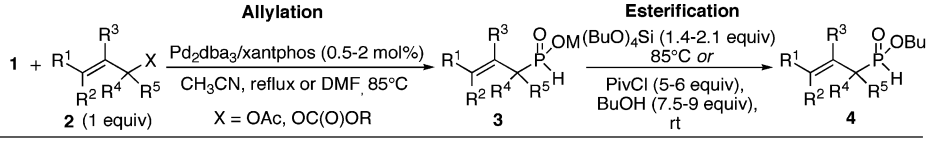
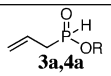
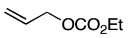
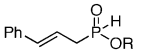
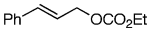
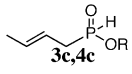
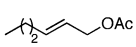
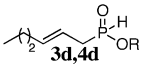
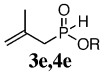
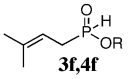
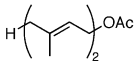
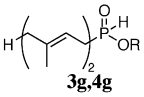
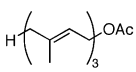
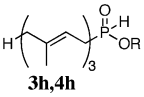
TABLE 3. Pd-Catalyzed Allylation and Tandem Allylation−Esterification with Activated Allylic Electrophiles[a]



entry	**1**[b] (equiv)	substrate **2**	solvent	product	% yield **3** (R=H)[c]	esterification $(RO)_4Si$ or ROH-PivCl	% yield **4** (R=Bu)
1	**1d** (2.5)		DMF	 **3a,4a**	62	BuOH	57
2	**1b** (3)		DMF	**4a**	-	$(BuO)_4Si$	52
3a	**1d** (3)		DMF		86	-	-
3b	**1a** (2)		CH_3CN	 **3b,4b**	100	$(BuO)_4Si$	67
3c	**1b** (3)		CH_3CN		-	$(BuO)_4Si$	91
4	**1d** (3)		DMF	**4b**	-	$(BuO)_4Si$	54
5	**1d** (2.5)		DMF	 **3c,4c**	69	BuOH	57
6a	**1d** (2.5)		DMF	 **3d,4d**	93	BuOH	68
6b	**1b** (3)		CH_3CN		-	$(BuO)_4Si$	45
7	**1d** (3)		DMF	 **3e,4e**	63	$(BuO)_4Si$	48
8a	**1d** (3)		DMF		88	-	-
8b	**1b** (3)		CH_3CN	 **3f,4f**	-	$(BuO)_4Si$	88
9a	**1d** (2.5)		DMF		-	BuOH	60
9b	**1b** (3)		CH_3CN		-	$(BuO)_4Si$	91
10a	**1d** (3)		DMF		100	BuOH	65
10b	**1c** (2.5)		DMF		85	-	-
10c	**1e** (3)		DMF	 **3g,4g**	63	-	-
10d	**1a** (3)		DMF		99	-	-
10e	**1a** (3)[e]		CH_3CN		100	$(BuO)_4Si$	58
10f	**1b** (3)		DMF		-	BuOH	70
10g	**1b** (3)		CH_3CN		-	$(BuO)_4Si$	75
11a	**1d** (3)		DMF	 **3h,4h**	100	-	-
11b	**1b** (3)		CH_3CN		-	$(BuO)_4Si$	62

[a] See the Experimental Section for details of the procedures. [b] **1a**: H_3PO_2. **1b**: $PhNH_3OP(O)H_2$. **1c**: $NH_4OP(O)H_2$. **1d**: $Et_3NHOP(O)H_2$. **1e**: *N*-ethylpiperidinium hypophosphite. [c] Isolated after extractive workup. [d] Isolated after chromatography purification. [e] 1 equiv of Et_3N was added.

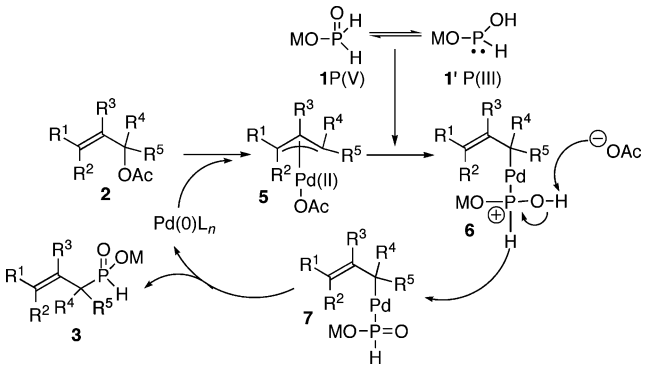
nearly quantitative formation of the allylation product (cinnamyl *H*-phosphinic acid) was observed, instead of the expected reduced product.

Gas chromatography analyses further proved this direct coupling and revealed complete disappearance of the acetate starting material after just 1 h, along with traces of the transfer hydrogenation product *β*-methylstyrene (4%). We soon found that $PdCl_2(PPh_3)_2$ was in fact unnecessary and that as low as 0.5 mol % of Pd_2dba_3/xantphos efficiently catalyzes this cross-coupling.

To determine the scope of the reaction, various allylic acetates were reacted with anilinium hypophosphite **1b**; however, the isolation of pure allylic-*H*-phosphinic acids **3** by extractive workup required prolonged stirring with Amberlite-H^+ resin and residual aniline was still difficult to remove completely. Thus, we thought that the hypophosphite salt of a more basic amine (ammonium hypophosphite $NH_4OP(O)H_2$, **1c**, and triethylammonium hypophosphite $Et_3NHOP(O)H_2$, **1d**) could substantially improve the isolation of products due to more efficient protonation during the workup. As can be seen in Table 3, triethylammonium hypophosphite **1d** turned out to be the most generally useful starting material, although ammonium hypophosphite **1c** and the commercially available, but highly hygroscopic and low-melting, *N*-ethylpiperidinium hypophosphite **1e** also furnished the products in good yields. H_3PO_2 **1a** effectively cross-coupled only with the reactive electron-poor cinnamyl acetate in CH_3CN in the absence of base (Table 3, entry 3b). However, with an aliphatic allylic acetate (entry 11e), **1a** did not react efficiently, and the addition of a base was needed for the reaction to be successful through in situ formation of **1d**.

The effectiveness of one-pot tandem cross-coupling−esterification processes for the direct synthesis of *H*-phosphinate butyl esters **4** was also demonstrated (Table 3). The reaction consists of an in situ esterification of the allylic *H*-phosphinic acids or their corresponding amine salts with tetrabutoxysilane[17] or using

SCHEME 2. Postulated Mechanism for the Cross-Coupling of Allylic Acetates

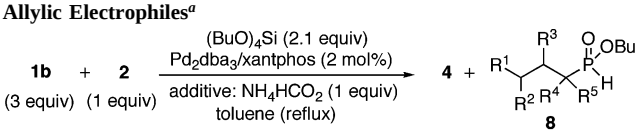


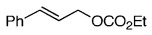
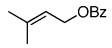
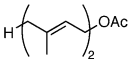
pivaloyl chloride in presence of *n*-BuOH.[18] A wide range of *H*-phosphinate esters were thus obtained in moderate to good yields after isolation by column chromatography over silica gel. When using tetrabutoxysilane, there was no need for prior acidification, solvent change, or an increase in the temperature to prepare the ester products in acceptable yields. This contrasts with our previous study of the alkoxysilane-promoted esterification of *H*-phosphinic acids, in which it was found that pure salts do not esterify efficiently.[17] Thus, the present methodology allows access to a wide range of allylic-*H*-phosphinic acids and/or their corresponding esters with complete regio- and stereocontrol.

In terms of allylic electrophiles **2**, we focused mainly on acetates since they are the more desirable starting materials, but a few examples of carbonates and benzoates (Table 3, entries 2, 4, and 9) were also secured. When using benzoates (entry 9), in situ esterification of the intermediate salt was required for isolation. 2-Substituted allylic acetates bearing electron-donating substituents did participate effectively in this transformation (entry 7), contrary to the results obtained in the allylation with allylic alcohols. Unfortunately, allylic acetates which are substituted at both the 1- and 3-positions, such as *trans*-1,3-diphenyl-2-propen-1-yl acetate and 2-cyclohexenyl acetate, reacted very sluggishly or not at all.

The proposed mechanism for this transformation is shown in Scheme 2. Allylic acetate **2** reacts with the Pd catalyst, which is generated in situ by reduction of the Pd(II) complex to Pd(0), affording the π-allylpalladium intermediate **5**. Intermolecular nucleophilic substitution of the P(III) form of the hypophosphorous compound **1′** takes place at the π-allyl system to give intermediate **6**, which in turn reacts with an acetate anion yielding intermediate **7**. Reductive elimination then produces the allylic-*H*-phosphinic acid derivative (**3**, M = H, R_3NH) and Pd(0). The fact that H_3PO_2 **1a** did not require added base when the reaction was performed in DMF (Table 3, entry 11d vs 11e) may be due to slow formation of a catalytic amount of dimethylamine from DMF upon acid catalysis and heating (85 °C). According to the postulated mechanism in Scheme 2, this basic additive may serve to drive the tautomeric equilibrium toward the P(III) form of the hypophosphorous compound **1′**, scavenge the AcOH released, and/or accelerate the formation of the active catalyst through reduction of Pd(II) back to Pd(0). As expected, the cross-coupling of D_3PO_2 with cinnamyl acetate shows no deuterium incorporation in the carbon backbone, thus confirming (along with our earlier GC studies) that the reaction occurs via a direct-coupling pathway.

TABLE 4. Direct One-Pot Allylation of Alkyl Phosphinates with Allylic Electrophiles[a]



entry	2	additive (equiv)	4	^{31}P NMR yield (%)[b] 4	8	% yield 4[c]
1a		0	**4a**	58	0	40
1b		1		67	0	48
2a		0	**4b**	52	0	-
2b		1		81	0	68
3a		0	**4f**	93	7	54
3b		1		97	3	61
4a		0	**4g**	48	9	-
4b		1		80	0	52

[a] Reactions were conducted in refluxing reagent grade toluene for 10−16 h under N_2. Details can be found in the Experimental Section. [b] Yields were determined on the crude reaction mixture. [c] Isolated yield after purification by silica gel chromatography. [d]Contains 7% of reduced product **8**.

We also evaluated a direct synthesis of allylic *H*-phosphinate esters **4** as previously described for the coupling with aryl/alkenyl electrophiles. As can be seen in Table 4, in this case, there is a marked tendency for the formation of significant amounts of byproducts **8** bearing a reduced double bond, as was observed with allylic halides. This also makes the isolation of pure allylic *H*-phosphinates problematic. In addition, the esterification often did not proceed to completion, considerably reducing the yields. The additive HCO_2NH_4 in toluene proved to be particularly useful in improving yields and/or decreasing the formation of **8**, but the reasons for this effect are unclear at this time. Overall, the one-pot coupling/esterification synthesis of *H*-phosphinate esters (Table 3) is considerably more robust and efficient than this process, so the investigation was not pursued further.

Pd-Catalyzed Rearrangement of Allylic Phosphinates toward the Development of a Direct Pd-Catalyzed Allylation of Hypophosphorous Acid with Allylic Alcohols. Based on the mechanism shown in Scheme 2, and guided by the prospect of maximizing efficiency, we then considered allylic alcohols **9** as coupling partners. Considering the analogy between allylic acetate **2** (Scheme 2) and allylic phosphinate **10** (Scheme 3), the development of a catalytic dehydrative allylation process became an intriguing possibility.

Considering that the pK_a of H_3PO_2 (1.3) is significantly lower than the pK_a of AcOH (4.76), a phosphinate must be better leaving group than an acetate, and therefore, oxidative addition must be possible. Scheme 3 shows how after oxidative addition into the C−O bond, intermediate **7** (which was also postulated in Scheme 2) can ultimately be produced and then generate

(17) Dumond, Y. R.; Baker, R. L.; Montchamp, J.-L. *Org. Lett.* **2000**, *2*, 3341.

(18) Representative examples of esterification of *H*-phosphinic acids with activating agents: (a) RCOCl/alcohol: (a) Bravo-Altamirano, K.; Montchamp, J.-L. *231st National Meeting of the American Chemical Society*, Atlanta, March 26−31, 2006; Poster 313. (b) Qiao, L.; Nan, F.; Kunkel, M.; Gallegos, A.; Powis, G.; Kozikowski, A. P. *J. Med. Chem.* **1998**, *41*, 3303. Carbodiimides: (c) Karanewsky, D. S.; Badia, M. C. *Tetrahedron Lett.* **1986**, *27*, 1751.

SCHEME 3. Capitalizing on the Analogy between Allylic Acetates and Allylic Phosphinates

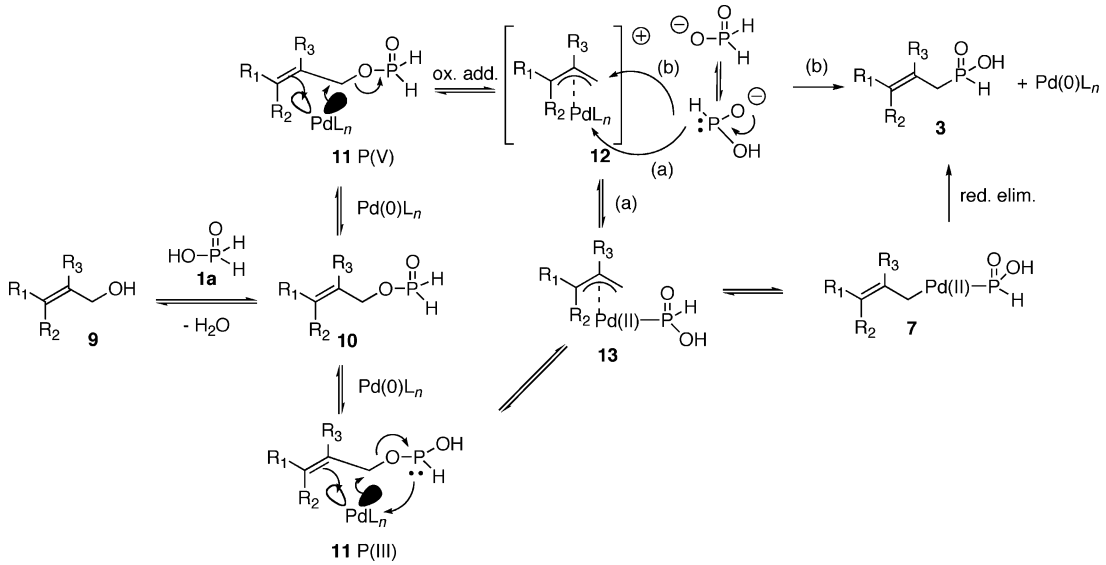
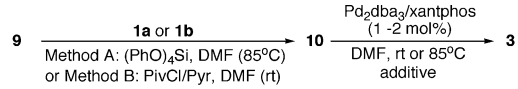
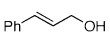
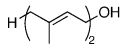


TABLE 5. Palladium-Catalyzed Rearrangement of Allylic Phosphinates[a]



entry	9	A/B[b] 10	% yield[c] 10	additive (equiv)	% NMR yield[c] (% isolated yield) 3
1a		A	91	H_3PO_2 (0-1)	11
1b				Et_3N (0.25)	52
2a		A	76	none	67 (58)
2b[e]		A	76	H_3PO_2 (1)	100 (72)
2c		B	100	H_3PO_2 (1)	98 (77)
3[e]		A	77	none	78 (59)

[a] Details of the procedures and esterification methods can be found in the Experimental Section. [b] Esterification method used to prepare **10**: method A, $(PhO)_4Si$; method B, PivCl. [c] Determined on the crude reaction mixture. [d] Isolated as **4** after esterification with $(BuO)_4Si$ and chromatographic purification. [e] Reactions conducted at rt.

allylic-*H*-phosphinic acid **3** through reductive elimination. The top pathway, through **11** P(V), is exactly analogous to other oxidative additions of allylic electrophiles with formation of an ion pair **12**, which can then form **13** through nucleophilic attack of the phosphorus atom at palladium (path a) or **3** through attack at the π-allyl terminus (path b). The bottom pathway, through **11** P(III), could also be operative to produce **13**. As long as Fisher esterification of **9** with H_3PO_2 **1a** can produce some amount of the allyl phosphinate **10**, the irreversible reductive elimination (**7** to **3**) or attack of the π-allyl (**12** to **3**) would drive the equilibrium. Indeed, we recently communicated (eq 2) the successful implementation of this novel reaction.[10]

Below we report further details on our dehydrative allylation as well as a full study of the one-pot synthesis of allylic *H*-phosphinate esters using this approach. Our initial entry into this project consisted of testing the hypothesized Pd-catalyzed overall rearrangement from **10** to **3**, with preformed allylic phosphinates (Table 5). Phosphinates **10** were synthesized from an allylic alcohol **9**, via transesterification of phenyl phosphinate,[19] or using pivaloyl chloride as an activating agent.[20] Compounds **10** were then reacted in situ with Pd/xantphos using DMF as a solvent. Rearrangement to *H*-phosphinic acid **3** was observed in moderate to good yields. With the simple allyl phosphinate, only low yields of rearranged product were observed, even with excess **1a** (Table 5, entry 1a). However, addition of a small amount of Et_3N (entry 1b) significantly improved the yield. The rationale for introduction of an acidic or basic additive was to catalyze the P(V) to P(III) tautomeric equilibrium in case the P(III) form **11** leads to more efficient oxidative addition and/or to facilitate the formation of **13** from **12** (Scheme 3). Both cinnamyl and geranyl allylic phosphinates **10** (entries 2a and 3) furnished the expected product **3** without additive. As shown in entries 2b and 2c, the use of an acid additive does improve the yields of products. Remarkably, the rearrangement even occurs at room temperature (entries 2b and 3). Two facts rule out a thermal[2,3] sigmatropic rearrangement[21] pathway: no reaction takes place in the absence of catalyst and the rearrangement of allylic phosphinates from primary alcohols provides exclusively primary *H*-phosphinic acids. Unfortunately, allylic phosphinates derived from secondary allylic alcohols did not participate in the reaction under any of the conditions investigated.

Once these experiments established the feasibility of the rearrangement, the environmentally friendly and atom-economical allylation reaction of H_3PO_2 with allylic alcohols could be developed (eq 2).[10] Although the Fisher esterification **9** to **10** (Scheme 3) must be operative, we could not detect the presence of **10** in the reaction mixture. The mechanism postulated in Scheme 3 is consistent with both the rearrangement studies of

(19) Deprèle, S.; Montchamp, J.-L. *J. Organomet. Chem.* **2002**, *643*−*644*, 154.

(20) (a) Bravo-Altamirano, K.; Montchamp, J.-L. Phosphinic Acid, Alkyl Esters. In *Encyclopedia of Reagents for Organic Synthesis* (eEROS), 2007. (b) Montchamp, J.-L. *J. Organomet. Chem.* **2005**, *690*, 2388. (c) Stawinski, J.; Thelin, M.; Westman, E.; Zain, R. *J. Org. Chem.* **1990**, *55*, 3503.

(21) (a) Mark, V. In *Mechanisms of Molecular Migrations*; Thyagarajan, B. S., Ed.; Interscience: New York, 1969; Vol. 2, pp 319−437. The rearrangement of propargyl phosphinates is also well-known: (b) Ionin, B. I.; Petrov, A. A. *Phosphorus, Sulfur, Silicon* **1990**, *49/50*, 243. (c) Belakhov, V. V.; Yudelevich, V. I.; Komarov, E. V.; Ionin, B. I.; Komarov, V. Y.; Zakharov, V. I.; Lebedev, V. B.; Petrov, A. A. *J. Gen. Chem. USSR* **1983**, *53*, 1345.

SCHEME 4. Pd-Catalyzed Dehydrative Allylation en Route to *P*-Heterocycles

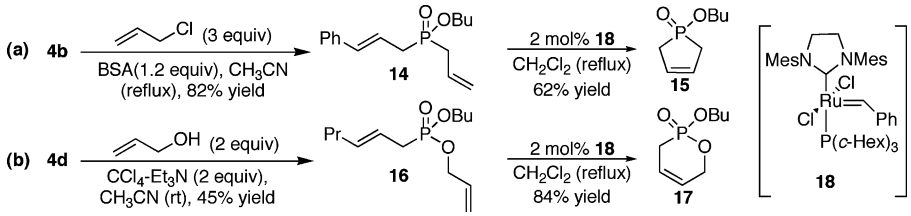
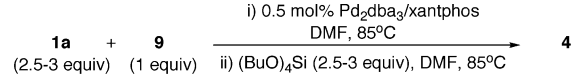
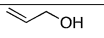
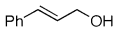
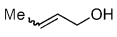
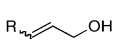
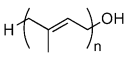
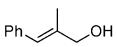
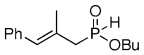
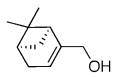
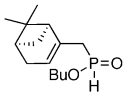
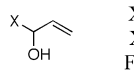
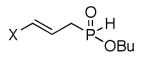


TABLE 6. Tandem Pd-Catalyzed Allylation−Esterification of H_3PO_2 with Allylic Alcohols[a]



entry	9	4	% yield 4[b]
1		**4a**	43[c]
2		**4b**	98
3		**4c**	88
4a	 R=*E*-Pr	**4d**	68
4b	=*Z*-Pr	**4d**	98
5a	 n=1	**4f**	52
5b	n=2	**4g**	64
5c	n=3	**4h**	72
6			57
7			58
8a	 X=Et		53
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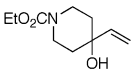
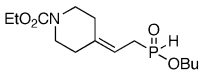
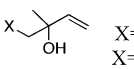
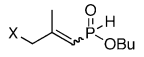
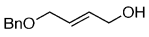
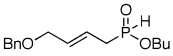
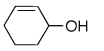
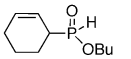
9			61
10a	 X=H		68
10b	X=prenyl		50
10c	X=geranyl		90
11			67
12			45[c,e]

[a] Reactions were conducted with concd H_3PO_2 in dry DMF (0.2 M). Reaction times: allylation = 2−8 h, esterification = 10−16 h. See the Experimental Section for details of the procedures. [b] Isolated yield after silica gel chromatography. [c] 2 mol % of Pd/xantphos. [d] 1:1 mixture of isomers. [e] DMF (2 M).

preformed **10**, the influence of additives, and the fact that addition of water slows down the reaction.

We then investigated the application of the dehydrative allylation to the synthesis of allylic *H*-phosphinate butyl esters **4** through a tandem allylation−esterification sequence (Table 6). As can be observed in Table 6, tetrabutoxysilane was used as the esterifying agent,[17] and the products were isolated with very good regio- and stereoselectivities after silica gel chromatography. Even some secondary 1,3-disubstituted allylic alcohols reacted in moderate yield. The yields of butyl esters are comparable to those achieved with the corresponding acids.[10]

Compared to the yields obtained through cross-coupling of allylic acetates (Table 3), the dehydrative allylation-esterification generally gives higher yields of the same products and proceeds from the more readily available alcohol starting materials. However, in the case of allyl-*H*-phosphinate (Table 3, entry 1 versus Table 6, entry 1) and methallyl-*H*-phosphinate (Table 3, entry 7), the cross-coupling approach is superior. Methallyl alcohol, like most 2-substituted allylic alcohols, does not react satisfactorily in the dehydrative allylation reaction.

Finally, the preparation of phosphorus heterocycles through ring-closing metathesis (RCM) from precursors prepared via allylation was briefly investigated (Scheme 4).[22] *H*-Phosphinates butyl esters **4b** and **4d** (Table 6) were prepared by tandem allylation−esterification reactions and then converted into the corresponding disubstituted phosphinate **14** and phosphonate **16**, via Arbuzov-like allylation[23] and Atherton−Todd oxidation,[24] respectively. Next, **14** and **16** were subjected to RCM to give *P*-heterocyclic products **15** and **17** in 50% and 37% overall yields (from H_3PO_2, **1a**), respectively. Mioskowski and coworkers[25] previously prepared the benzyloxy and the hydroxy analogues of the butoxy phospholene oxide **15** in 27% and 62% yields (from $NH_4OP(O)H_2$, **1c**) following a RCM strategy and using a nucleophilic substitution of bis(trimethylsiloxy)phosphine (BTSP, $(TMSO)_2PH$) with allylic halides for the C−P bond formation. The cyclic allylphosphonate **17** is a new compound; however, its methyl ester counterpart has been previously prepared in 9.8% yield via reaction of diphenyl phosphoryl chloride with allylmagnesium bromide, followed by selective displacement of one of the phenoxy groups with lithium allyloxide and RCM.[26]

Conclusion

The Pd-catalyzed dehydrative allylation of H_3PO_2 with allylic alcohols is the most general and convenient catalytic method available to access allylic-*H*-phosphinic acids and their ester derivatives, followed by the reaction of allylic acetates. These methods are by far superior to previously known approaches, such as the base-promoted allylation of alkyl phosphinates, the Michaelis−Becker reaction of masked hypophosphorous synthons, and the reaction of allylic halides with bis(trimethysiloxy)phosphine which not only involves wasteful silylation and a halide-containing electrophile but tends to form symmetrically disubstituted products. The hydrophosphinylation approach to

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allylic-*H*-phosphinates from allenes, conjugated dienes, and enynes is not viable because regio- and stereochemical complications arise, leading to mixture of products. The starting materials are also much less accessible than allylic alcohols and their derivatives. One possible exception exists in the case of isoprene.

With the development of transition-metal-catalyzed reactions (Pd, Ni) of hypophosphorous compounds, a wide variety of *H*-phosphinic acid and esters is now available. Allylic alcohols and acetates join the ranks of aryl, alkenyl, and benzylic halides, as well as alkenes and alkynes in the list of useful starting materials for the syntheses of *H*-phosphinate compounds.

Experimental Section

Representative Procedure for the Hydrophosphinylation of Allenes (Table 1, Entry 2a). To a solution of concd **1a** (obtained by rotary evaporation (0.5 mmHg) of the 50 wt % aqueous solution at rt for 20−30 min before reaction) (0.264 g, 4 mmol) in CH_3CN (10 mL) were added 1-phenylallene[11] (0.232 g, 2 mmol), Pd_2dba_3 (0.0092 g, 0.01 mmol, 1 mol % Pd), and xantphos (0.0127 g, 0.022 mmol, 0.011 equiv) at rt. The resulting mixture was heated at the reflux temperature of CH_3CN under N_2 for 12 h. Reaction progress was conveniently monitored by ^{31}P NMR analysis, although TLC or GC analysis using an internal standard are also viable alternatives. After the mixture was cooled to rt, ^{31}P NMR analysis showed quantitative formation of the expected product (δ: 36 ppm) as a doublet in the $^{31}P-^{1}H$ coupled spectrum. The mixture was diluted with EtOAc and washed with 2 M aq HCl. The aqueous phase was extracted with EtOAc and the combined organic fractions were washed with brine. Drying over $MgSO_4$ and concentration afforded cinnamyl-*H*-phosphinic acid **3b**[10] (0.364 g, 2 mmol, 100% yield) as a light yellow solid: mp 85 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 10.45 (bs, 1H), 7.18−7.42 (m, 5H), 7.04 (d, J_{HP} = 558 Hz, 1H), 6.53 (dd, J = 15.8 Hz, J = 5.3 Hz, 1H), 6.02−6.18 (m, 1H), 2.77 (dd, J_{HP} = 19.3 Hz, J = 7.0 Hz, 2H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 136.7 (d, J_{PCCCC} = 4.0 Hz, C), 136.3 (d, J_{PCCC} = 14.7 Hz, CH), 128.8 (2xCH), 128.1 (CH), 126.6 (2 × CH), 117.0 (d, J_{PCC} = 10.1 Hz, CH), 34.7 (d, J_{PC} = 91.0 Hz, CH_2); ^{31}P NMR (121.47 MHz, $CDCl_3$) δ 35.32 (dm, J_{PH} = 558 Hz); IR (thin film, KBr), cm^{-1} 2621 and 1688 (P−O−H); 2422, 2292 and 2181 (P−H); and 1241 (P═O); UV (EtOH, C = 8 μM) λ_{max} = 274 nm; HRMS (EI^+) *m*/*z* calcd for $C_9H_{11}O_2P$ 182.0495, found 182.0497. Anal. Calcd for $C_9H_{11}O_2P$: C, 59.34; H, 6.09. Found: C, 59.04; H, 6.02.

Representative Procedure for the Hydrophosphinylation of Dienes (Table 2, Entry 1). To a solution of **1b** (0.955 g, 6 mmol, 3 equiv) in DMF (10 mL) was added isoprene (0.20 mL, 0.136 g, 2 mmol, 1 equiv), followed by Pd_2dba_3 (0.0092 g, 0.01 mmol, 1 mol % Pd) and xantphos (0.0127 g, 0.022 mmol, 0.011 equiv) at rt. The resulting mixture was heated at 85 °C in an oil bath during 10 h. ^{31}P NMR analysis indicated the formation of the product (δ: 26 ppm) as a doublet in the $^{31}P-^{1}H$-coupled spectrum, along with complete disappearance of **1b**. The crude reaction mixture was concentrated by rotary evaporation (40 °C, 0.5 mmHg) for 30 min, and the residue was diluted with EtOAc and washed with 2 M aq HCl. The organic layer was extracted with EtOAc, and the combined organic fractions were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was dissolved in CH_2Cl_2, and Amberlite resin (4−5 tips of scoopula) was added. The resulting suspension was stirred for 12 h at rt and then suction-filtered in a Büchner funnel and concentrated to give **3f**[10] as a clear oil (0.153 g, 1.14 mmol, 57% yield): ^1H NMR ($CDCl_3$, 300 MHz) δ 10.91 (bs, 1H), 6.94 (d, J_{HP} = 550 Hz, 1H), 5.13 (qq, J = 7 Hz, J = 2 Hz, 1H), 2.57 (dd, J_{HP} = 19 Hz, J = 8 Hz, 2H), 1.77 (d, J = 6 Hz, 3H), 1.66 (d, J = 4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 138.4 (d, J_{PCCC} = 14 Hz), 110.6 (d, J_{PCC} = 9 Hz), 30.1 (d, J_{PC} = 92 Hz), 25.8 (d, J_{PCCCC} = 3 Hz), 18.2 (d, J_{PCCCC} = 3 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 35.86 (dm, J_{PH} = 550 Hz); HRMS (EI^+) *m*/*z* calcd for $C_5H_{11}O_2P$ ($[M]^+$) 134.0497, found 134.0494.

Representative Procedures for the Allylation Reaction with Activated Allylic Electrophiles (Table 3). (a) Synthesis of 3b from H_3PO_2 (Entry 3b). To a solution of freshly concentrated **1a** (0.264 g, 4 mmol) in CH_3CN (10 mL) were added cinnamyl acetate (0.352 g, 0.33 mL, 2 mmol), Pd_2dba_3 (0.0046 g, 0.005 mmol), and xantphos (0.0064 g, 0.011 mmol) at rt. The reaction was heated at 85 °C under N_2 for 15 h. At that time, ^{31}P NMR analysis revealed quantitative formation of the product (δ 33.2 ppm). The solution was diluted with EtOAc and washed with 2 M aq $NaHSO_4$. The aqueous layer was separated and extracted with EtOAc, and the combined organic fractions were washed with brine. Drying and concentration furnished the acid **3b**[10] in quantitative yield as a light yellow solid (0.364 g, 2 mmol).

(b) Synthesis of 3g from a Salt of H_3PO_2 (Entry 10a). To a solution of triethylammonium hypophosphite **1d** (1.0 g, 6 mmol, 3 equiv) in DMF (10 mL) were added *trans*-geranyl acetate (0.43 mL, 0.393 g, 2 mmol, 1 equiv), Pd_2dba_3 (0.0046 g, 0.005 mmol), and xantphos (0.0064 g, 0.011 mmol) at rt. The reaction was heated at 85 °C under N_2 for 2 h. After the mixture was cooled to rt, ^{31}P NMR analysis revealed quantitative formation of the allylation product (δ 23.7 ppm). The mixture was concentrated under high vacuum, and the residue was diluted with EtOAc, and washed with 2 M aq HCl. The aqueous phase was extracted with EtOAc, and the combined organic fractions were washed with brine, dried over $MgSO_4$, and concentrated. The residue was dissolved in CH_2Cl_2 (10 mL), treated with Amberlite resin (4−5 tips of scoopula) at rt for 12 h, and then suction-filtered to furnish 100% yield of **3g**[10] (0.404 g, 2 mmol, 100% yield) as a light yellow oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 11.39 (bs, 1H), 6.94 (dt, J_{HP} = 552 Hz, J= 2 Hz, 1H), 5.0 − 5.21 (m, 2H), 2.60 (dd, J_{HP} = 19 Hz, J = 8 Hz, 2H), 2.0−2.18 (m, 4H), 1.68 (s, 3H), 1.66 (d, J = 4 Hz, 3H), 1.60 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 142.3 (d, J_{PCCC} = 14 Hz), 132.0, 124.0, 110.6 (d, J_{PCC} = 9 Hz), 39.9 (d, J_{PCCCC} = 3 Hz), 30.2 (d, J_{PC} = 92 Hz), 26.7 (d, J_{PCCCCC} = 4 Hz), 25.9, 17.9, 16.7 (d, J_{PCCCC} = 3 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 37.10 (dm, J_{PH} = 552 Hz); HRMS (EI^+) calcd for $C_{10}H_{19}O_2P$ ($[M]^+$) 202.1123, found 202.1122.

(c) Synthesis of 4f via Tandem Allylation−Esterification Using $(RO)_4Si$ (Entry 9b). To a suspension of anilinium hypophosphite **1b** (0.955 g, 6 mmol) in CH_3CN (10 mL) were added prenyl benzoate (0.38 mL, 0.385 g, 2 mmol), Pd_2dba_3 (0.0184 g, 0.02 mmol), and xantphos (0.0254 g, 0.044 mmol). The mixture was heated at reflux for 8 h and then cooled to rt. To the reaction mixture was added $(BuO)_4Si$ (1.40 g, 4.2 mmol), and the reaction was returned to reflux and kept at this temperature for 16 h. The resulting mixture was then diluted with EtOAc and washed with 2 M aq HCl. The aqueous phase was extracted with EtOAc, and the organic layer was washed with saturated aq $NaHCO_3$ and brine. Drying over $MgSO_4$, concentration, and purification by radial chromatography (4 mm thickness, hexanes/EtOAc 7/1, v/v, EtOAc) afforded **4f**[9] as a clear oil (0.346 g, 1.82 mmol, 91% yield): ^1H NMR ($CDCl_3$) δ 7.04 (d, J_{HP} = 538 Hz, 1H), 5.07−5.16 (m, 1H), 4.01 and 4.10 (dtd, J = 11 Hz, J = 8 Hz, J_{HP} = 7 Hz, 2H), 2.55−2.66 (m, 2H), 1.77 (d, J = 7 Hz, 3H), 1.59−1.72 (m, 5H), 1.40 (sext, J = 8 Hz, 2H), 0.95 (t, J = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 138.3 (d, J_{PCCC} = 14 Hz), 110.7 (d, J_{PCC} = 14 Hz), 66.4 (d, J_{POC} = 8 Hz), 32.7 (d, J_{POCC} = 6 Hz), 29.8 (d, J_{PC} = 92 Hz), 26.0 (d, J_{PCCCC} = 4 Hz), 18.7, 18.1 (d, J_{PCCCC} = 4 Hz), 13.8; ^{31}P NMR ($CDCl_3$) δ 38.01 (d, J_{PH} = 538 Hz); HRMS (EI^+) calcd for $C_9H_{19}O_2P$ ($[M]^+$) 190.1123, found 190.1127.

(d) Synthesis of 4d via Tandem Allylation−Esterification Using PivCl/ROH (Entry 6a). To a 25 mL round-bottom flask charged with triethylammonium hypophosphite **1d** (0.835 g, 5 mmol) and DMF (10 mL) were added *trans*-2-hexenyl acetate (0.32 mL, 0.284 g, 2 mmol), Pd_2dba_3 (0.0046 g, 0.005 mmol), and xantphos (0.0064 g, 0.011 mmol) under nitrogen. The resulting

mixture was heated at 85 °C for 6 h. ^{31}P NMR analysis of the crude mixture indicated quantitative formation of the product (δ 25 ppm). After the mixture was cooled to rt, BuOH (1.4 mL, 1.11 g, 15 mmol) and pivaloyl chloride (1.3 mL, 1.206 g, 10 mmol) were added, and the reaction was stirred for 6 h under N_2, diluted with EtOAc, and washed with 2 M aq $NaHSO_4$. The aqueous layer was extracted with EtOAc, and the combined organic fractions were washed with saturated aq $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography on silica gel (hexanes/EtOAc 3/1, v/v, EtOAc) to afford **4d** as a clear oil (0.277 g, 1.36 mmol, 68% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.95 (dt, J_{HP} = 540 Hz, J = 2 Hz, 1H), 5.63 (dt, J = 22 Hz, J = 7 Hz, 1H), 5.33 (dt, J = 22 Hz, J = 7 Hz, 1H), 4.0 and 4.12 (dtd, J = 11 Hz, J = 8 Hz, J_{HP} = 7 Hz, 2H), 2.59 (dd, J_{HP} = 19 Hz, J = 7 Hz, 2H), 2.03 (t, J = 7 Hz, 2H), 1.68 (quint, J = 7 Hz, 2H), 1.3−1.5 (m, 4H), 0.94 (t, J = 7 Hz, 3H), 0.90 (t, J = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 137.8 (d, J_{PCCC} = 14 Hz), 116.7 (d, J_{PCC} = 9 Hz), 66.4 (d, J_{POC} = 7 Hz), 34.9 (d, J_{PCCCC} = 3 Hz), 33.5 (d, J_{PC} = 91 Hz), 32.6 (d, J_{POCC} = 6 Hz), 22.4 (d, J_{PCCCCC} = 4 Hz), 18.9, 13.8, 13.7; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 39.14 (dt, J_{PH} = 540 Hz, J = 5 Hz); HRMS (EI^+) calcd for $C_{10}H_{21}O_2P$ ($[M]^+$) 204.1279, found 204.1281.

Representative Procedure for the Direct One-Pot Allylation of Alkyl Phosphinates (Table 4, Entry 4b). To a suspension of **1b** (0.955 g, 6 mmol) and $(BuO)_4Si$ (1.346 g, 4.2 mmol) in toluene (12 mL) were added *trans*-geranyl acetate (0.43 mL, 0.393 g, 2 mmol) and NH_4HCO_2 (0.126 g, 2 mmol) followed by Pd_2dba_3 (0.0184 g, 0.02 mmol) and xantphos (0.0254 g, 0.044 mmol) at rt. The reaction was heated at reflux for 10 h. After the mixture was cooled to rt, ^{31}P NMR analysis showed the product at δ 38.9 ppm. The mixture was diluted with EtOAc and washed with 2 M aq $NaHSO_4$. The aqueous phase was extracted with EtOAc, and the combined organic fractions were washed with saturated aq $NaHCO_3$ and brine. Drying, concentration, and purification by radial chromatography (4 mm thickness, hexanes/EtOAc 9/1, v/v, EtOAc) afforded **4g**[9] as a clear yellow oil (0.269 g, 1.04 mmol, 52% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.92 (ddd, J_{HP} = 537 Hz, J = 3 Hz, J = 2 Hz, 1H), 5.04−5.19 (m, 2H), 4.0 and 4.09 (dtd, J = 10 Hz, J = 8 Hz, J_{HP} = 7 Hz, 2H), 2.49−2.68 (m, 2H), 2.08 (s, 3H), 1.62−1.71 (m, 9H), 1.60 (s, 3H), 1.41 (sext, J = 7 Hz, 2H), 0.94 (t, J = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 142.2 (d, J_{PCCC} = 14 Hz), 131.9, 123.9, 110.5 (d, J_{PCC} = 9 Hz), 66.4 (d, J_{POC} = 7 Hz), 39.8 (d, J_{PCCCC} = 3 Hz), 32.6 (d, J_{POCC} = 6 Hz), 29.6 (d, J_{PC} = 92 Hz), 26.6 (d, J_{PCCCCC} = 4 Hz), 25.9, 18.9, 17.9, 16.7 (d, J_{PCCCC} = 3 Hz), 13.8; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 38.47 (dm, J_{PH} = 537 Hz); HRMS (EI^+) calcd for $C_{14}H_{27}O_2P$ ($[M]^+$) 258.1749, found 258.1747.

Representative Procedure for the Pd-Catalyzed Rearrangement of Allylic Phosphinates (Table 5, Entry 2a). To a solution of concd **1a** (0.132 g, 2 mmol, 1 equiv) in dry DMF (10 mL) were added $(PhO)_4Si$[27] (0.800 g, 2 mmol, 1 equiv) and cinnamyl alcohol (0.514 mL, 4 mmol, 2 equiv). The reaction was heated at 85 °C for 2 h. After the mixture was cooled to rt, ^{31}P NMR analysis showed the cinnamyl hypophosphite ester (**10**) at δ 14.32 ppm (76%). To the reaction mixture were added Pd_2dba_3 (0.0092 g, 0.01 mmol, 1 mol % Pd) and xantphos (0.0127 g, 0.022 mmol), and the resulting mixture was heated at 85 °C for 2 h or stirred at rt for 4 h to yield crude **3b.** The reaction was concentrated in vacuo, and the residue was diluted with EtOAc and washed with 2 M aq HCl. The aqueous phase was extracted with EtOAc, and the combined organic fractions were washed with brine, dried over $MgSO_4$, and concentrated. The residue was suspended in toluene (10 mL), and $(BuO)_4Si$ (0.641 g, 2 mmol, 1 equiv) was added at rt. The reaction was heated at reflux for 12 h, diluted with EtOAc, and washed with brine. Drying over $MgSO_4$, concentration, and purification by radial chromatography (4 mm thickness, hexanes/EtOAc 5:1, v/v, EtOAc) afforded **4b**[7d,9,10] as a clear yellow oil (0.276 g, 1.16 mmol, 58%): ^{1}H NMR ($CDCl_3$) δ 7.06 (dt, J_{HP} = 543 Hz, J = 2 Hz, 1H), 7.23−7.38 (m, 5H), 6.55 (dd, J = 16 Hz, J = 6 Hz, 1H), 6.06−6.17 (m, 1H), 4.03 and 4.13 (tdd, J = 10 Hz, J_{HP} = 7 Hz, J = 8 Hz, 2H), 2.82 (dd, J_{HP} = 19 Hz, J = 8 Hz, 2H), 1.65−1.74 (m, 2H), 1.42 (sext, J = 8 Hz, 2H), 0.94 (t, J = 7 Hz, 3H); ^{13} C NMR ($CDCl_3$) δ 136.6 (d, J_{PCCCC} = 4 Hz), 136.1 (d, J_{PCCC} = 14 Hz), 128.7 (2C), 128.0, 126.4 (2C), 116.9 (d, J_{PCC} = 10 Hz), 66.5 (d, J_{POC} = 7 Hz), 34.7 (d, J_{PC} = 90 Hz), 32.6 (d, J_{POCC} = 6 Hz), 18.9, 13.8; ^{31}P NMR ($CDCl_3$) δ 35.94 (dt, J_{PH} = 543 Hz, J = 7 Hz); HRMS (EI^+) calcd for $C_{13}H_{19}O_2P$ $(M)^+$ 238.1123, found 238.1126.

Representative Procedure for the Tandem Allylation−Esterification of H_3PO_2 with Allylic Alcohols (Table 6, Entry 1). To a DMF (10 mL) solution of concd **1a** (0.396 g, 6 mmol, 3 equiv) in a pressure tube fitted with a rubber septum were added allyl alcohol (0.14 mL, 0.116 g, 2 mmol, 1 equiv), Pd_2dba_3 (0.0184 g, 0.02 mmol, 2 mol % Pd), and xantphos (0.0254 g, 0.044 mmol) under N_2. The tube was tightly closed with the corresponding threaded Teflon plug and heated for 3 h in an oil bath at 85 °C and then cooled to rt. The Teflon plug was replaced by a septum, $(BuO)_4Si$ (2.1 mL, 1.923 g, 6 mmol, 3 equiv) was added, and the resulting mixture was heated at 85 °C for 14 h. ^{31}P NMR analysis then revealed the formation of **4a** at δ 37.2 ppm (63% NMR yield). The solution was diluted with EtOAc and washed with 2 M aq HCl. The aqueous phase was extracted with EtOAc, and the combined organic fractions were washed with saturated aq $NaHCO_3$ and brine. Drying over $MgSO_4$, concentration, and purification by flash column chromatography over silica gel (hexanes/EtOAc 1:1, v/v, EtOAc) afforded **4a**[9,10,28] as a colorless oil (0.140 g, 0.86 mmol, 43%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.00 (dt, J_{HP} = 543 Hz, J = 2 Hz, 1H), 5.68−5.82 (m, 1H), 5.20−5.31 (m, 2H), 4.03 and 4.13 (dtd, J = 10 Hz, J = 9 Hz, J_{HP} = 7 Hz, 2H), 2.66 (ddd, J_{HP} = 19 Hz, J = 8 Hz, J = 2 Hz, 2H), 1.64 − 1.74 (m, 2H), 1.42 (sext, J = 8 Hz, 2H), 0.95 (t, J = 8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 125.9 (d, J_{PCC} = 9 Hz), 121.5 (d, J_{PCCC} = 14 Hz), 66.5 (d, J_{POC} = 8 Hz), 35.0 (d, J_{PC} = 90 Hz), 32.6 (d, J_{POCC} = 6 Hz), 18.9, 13.8; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 37.79 (dm, J_{PH} = 543 Hz); HRMS (EI^+) calcd for $C_7H_{15}O_2P$ ($[M]^+$) 163.0888, found 163.0883.

Synthesis of *P*-Heterocycles via Pd-Catalyzed Dehydrative Allylation (Scheme 4). (a) 1-Butoxy-3-phospholene 1-Oxide (15). To a solution of concd **1a** (0.594 g, 9 mmol, 3 equiv) in dry DMF (15 mL) were added cinnamyl alcohol (0.39 mL, 0.403 g, 3 mmol), Pd_2dba_3 (0.0069 g, 0.0075 mmol), and xantphos (0.0095 g, 0.0165 mmol) at rt. The reaction was heated at 85 °C under N_2 for 1.5 h. After the mixture was cooled to rt, $(BuO)_4Si$ (3.2 mL, 2.88 g, 9 mmol, 3 equiv) was added, and the reaction mixture was heated at 85 °C for 12 h. The mixture was diluted with EtOAc and washed with 2 M aq HCl. The aqueous phase was extracted with EtOAc, and the combined organic fractions were washed with saturated aq $NaHCO_3$ and brine. Drying over $MgSO_4$, concentration, and purification by column chromatography over silica gel (hexanes/EtOAc 1:1, v/v, EtOAc) afforded 0.700 g (2.94 mmol) of **4b**, which was dissolved in anhyd CH_3CN (15 mL) and placed under N_2 in a pressure tube fitted with a rubber septum. To the resulting solution were added BSA (0.87 mL, 0.72 g, 3.53 mmol) and allyl chloride (0.72 mL, 0.675 g, 8.82 mmol). The reaction tube was closed with a Teflon plug and heated at 85 °C for 8 h. After the mixture was cooled to rt, ^{31}P NMR analysis revealed the formation of **14** (δ 49.9 ppm, 82% NMR yield). The reaction was quenched with saturated $NaHCO_3$ and extracted with EtOAc. The combined organic phases were washed with 2 M aq HCl and brine, dried over $MgSO_4$, and concentrated to give the crude product, which was dissolved in anhyd CH_2Cl_2 (150 mL), and [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)-

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(tricyclohexylphosphine)ruthenium **18** (0.0409 g, 0.0482 mmol) was added under N_2 at rt. The mixture was heated at reflux for 12 h and then allowed to cool to rt and treated with activated charcoal (0.250 g). The resulting suspension was stirred for 12 h ar rt, suction-filtered through a Celite pad in a Büchner funnel, and concentrated in vacuo. Purification by flash chromatography over silica gel (EtOAc, EtOAc/MeOH 90:10, v/v) afforded **15**[29] as a clear yellow oil (0.261 g, 1.5 mmol, 50% overall yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.98 (d, J = 34 Hz, 2H), 3.98−4.14 (m, 2H), 2.38−2.50 (m, 4H), 1.60−1.74 (m, 2H), 1.41 (sext, J = 8 Hz, 2H), 0.94 (t, J = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 127.2 (d, J_{PCC} = 16 Hz, 2C), 64.9 (d, J_{POC} = 7 Hz), 32.8 (d, J_{POCC} = 6 Hz), 29.3 (d, J_{PC} = 91 Hz, 2C), 19.0, 13.8; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 75.83.

(b) (3,6-Dihydro-2-butoxy-2-oxide)-2*H*-1,2-oxaphosphorin (17). To a solution of concd **1a** (0.594 g, 9 mmol) in dry DMF (15 mL) were added *cis*-2-hexenyl alcohol (0.36 mL, 0.300 g, 3 mmol), Pd_2-dba_3 (0.0069 g, 0.0075 mmol), and xantphos (0.0095 g, 0.0165 mmol) at rt. The reaction was heated at 85 °C under N_2 for 8 h and then allowed to warm to rt. $(BuO)_4Si$ (3.2 mL, 2.88 g, 9 mmol) was added, and the reaction was heated at 85 °C for another 12 h under N_2. The reaction was diluted with EtOAc and washed with 2 M aq HCl. The aqueous layer was extracted with EtOAc, and the combined organic fractions were washed with saturated aq $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated. The resulting oil was purified by silica gel chromatography (hexanes/EtOAc 1:1, v/v, EtOAc) to give 0.600 g (2.94 mmol) of **4d**, which was dissolved in anhyd CH_3CN (16 mL) and treated with anhyd CCl_4 (0.57 mL, 0.905 g, 5.88 mmol), allyl alcohol (0.40 mL, 0.342 g, 5.88 mmol), and Et_3N (0.82 mL, 0.595 g, 5.88 mmol, 2 equiv) at rt under N_2. The reaction was stirred for 12 h at rt. ^{31}P NMR analysis revealed the formation of **16** (δ = 29.4 ppm, 45% NMR yield). The reaction mixture was diluted with EtOAc and washed with 2 M aq HCl. The aqueous layer was extracted with EtOAc, and the combined organic layers were washed with saturated aq $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated. The crude **16** was dissolved in anhyd CH_2Cl_2 (130 mL) and treated with **18** (0.0225 g, 0.0264 mmol, 2 mol %). The reaction was heated at reflux for 14 h under N_2. After the mixture was cooled to rt, activated charcoal (0.130 g) was added, and the suspension was stirred for 12 h at rt. The mixture was then filtered through a Celite pad in a Büchner funnel and concentrated in vacuo to afford the crude product, which was purified by silica gel column chromatography (Hex/EtOAc 5:1, v/v, EtOAc) to give 0.211 g (1.11 mmol, 37% overall yield) of **17**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.63−5.89 (m, 2H), 4.70−4.93 (m, 2H), 4.04−4.23 (m, 2H), 2.36−2.69 (m, 2H), 1.60−1.77 (m, 2H), 1.34−1.52 (m, 2H), 0.94 (t, J = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 125.4 (d, J_{PCC} = 17 Hz), 120.7 (d, J_{POCC} = 10 Hz), 69.1 (d, J_{POC} = 8 Hz), 65.5 (d, J_{POC} = 7 Hz), 32.7 (d, J_{POCC} = 6 Hz), 22.5 (d, J_{PC} = 134 Hz), 18.9, 13.8; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 20.75.

Acknowledgment. We thank the National Institute of General Medical Sciences/NIH (1R01 GM067610, IAT, JLM) and the National Science Foundation (CHE-0242898, KBA) for the financial support of this research.

Supporting Information Available: General experimental procedures and detailed spectroscopic data (^{31}P, ^{1}H, and ^{13}C NMR spectra and HRMS data) for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO702542A

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