The Mechanism of Double Olefination Using Titanium-Substituted Ylides

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The adduct **3**, derived from $TiCl_3(O\textit{i}Pr)$ and $(Me_2N)_3P{=}CH_2$, engages in a complicated set of interactions with $NaN(SiMe_3)_2$ and aldehydes, resulting in the requirement to use excess amounts of both reagents for the one-pot synthesis of allenes. When $TiCl_2(O\textit{i}Pr)_2$ is used instead, ligand substitution reactions with $NaN(SiMe_3)_2$ are diminished and so stepwise transformations can be accomplished without excess amounts of each reagent. The selective production of vinylphosphonium salts and byproduct titanium oxides from Ti-substituted ylides and aldehydes is proposed to arise from the presence of a chloride leaving group on the metal. Isolated vinylphosphonium compounds may be deprotonated with phenyllithium to give thermally sensitive allenic phosphoranes, which have been characterized by low temperature multinuclear NMR. The reaction of allenic phosphoranes with aldehydes affords oxaphosphetane and betaine intermediates which appear to interconvert upon warming to produce allene and phosphine oxide. Dimethylamino-substituted phosphorus components are required for high yields in both steps of the allene-forming process, presumably to boost the reactivity of the hindered Ti-substituted ylide reagents and to stabilize the allenic phosphorane unit so that it may be trapped by aldehyde. The placement of chiral groups on the phosphorus methylide or aldehyde components results in low levels of enantiomeric and diastereomeric induction, respectively, during allene formation. In two cases, the diastereomeric ratios of initially-formed oxaphosphetanes have been found to differ from the diastereomeric composition of their product allenes, offering examples of the phenomenon known as “stereochemical drift”. However, oxaphosphetane/betaine formation from allenic phosphorane and aldehyde has been found to be irreversible, suggesting that an intramolecular betaine olefin isomerization is responsible for the loss of stereochemical integrity during the Wittig step.

In the accompanying paper,[1a] we report the convenient synthesis of vinylphosphonium salts and allenes from carbonyl compounds in a stepwise “double olefination” process employing a phosphorus−titanium reagent. Because of the importance of phosphine oxide and metal oxide elimination processes in organic synthesis, and because we wish to control the stereochemical aspects of allene formation, a detailed understanding of the double olefination mechanism is desirable. We report here the results of mechanistic studies, which include the observation or isolation of most of the intermediates in the process.

The reported chemistry of phosphorus ylide compounds bearing metal or metalloid substituents at the ylide carbon is dominated by lithiated[2] and silylated[3] species. Ylides with metallocene or other early transition metal substituents have been prepared,[4] but their reactions have received comparatively little attention. Particularly relevant are early reports which describe the production of allenes directly from the reaction of $SiMe_3$ substituted phosphorus methylides and ketones: vinylphosphonium salts are reported as intermediates,[3a] but substantial quantities of methylene alkenes are produced along with allenes.[3b] The compounds discussed here bear Ti(IV) alkoxy halide moieties, and therefore also act as “doubly oxophilic” reagents to produce allenes, with the important distinction that allene formation is dominant for a wide variety of nonenolizable substrates. A single example of a similar process using a boron-substituted ylide has been reported, but its scope was not explored.[5]

Results

One-Pot Condensation of Aromatic Aldehydes to Allenes.[1b] *Synthesis and Structure of the Allenating Agent.* We have previously reported, following the lead

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[1] (a) Reynolds, K. A.; Dopico, P. G.; Brody, M. S.; Finn, M. G. *J. Org. Chem.* **1997**, *62*, 2564−2573 (preceeding paper in this issue). (b) Reynolds, K. A.; Dopico, P. G.; Sundermann, M. J.; Hughes, K. A.; Finn, M. G. *J. Org. Chem.* **1993**, *58*, 1298−1299.

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[3] (a) Gilman, H.; Tomasi, R. A. *J. Org. Chem.* **1962**, *27*, 3647−3650. (b) Schmidbaur, H.; Stuhler, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 321−322. Schmidbaur, H.; Tronich, W. *Chem. Ber.* **1967**, *100*, 1032−1037. (c) Bestmann, H. J.; Bomhard, A.; Dostalek, R.; Pichl, R.; Riemer, R.; Zimmermann, R. *Synthesis* **1992**, 787−792. (d) Bestmann, H. J.; Dostalek, R.; Zimmermann, R. *Chem. Ber.* **1992**, *125*, 2081−2084. (e) Schmidbaur, H.; Pichl, R.; Muller, G. *Chem. Ber.* **1987**, *120*, 789−794. (f) Schmidbaur, H.; Wolf, W. *Chem. Ber.* **1975**, *108*, 2851−2856. (g) Schmidbaur, H.; Malisch, W. *Chem. Ber.* **1970**, *103*, 97−103. (h) Grützmacher, H.; Pritzkow, H. *Organometallics* **1991**, *10*, 938−946.

[4] (a) For reviews of metal-substituted ylide complexes, see: Schmidbaur, H. *Acc. Chem. Res.* **1975**, 62−70. Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907−927. Metallocene-substituted ylide chemistry: (b) Erker, G.; Czisch, P.; Mynott, R. *J. Organomet. Chem.* **1987**, *334*, 91−108. (c) Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Organometallics* **1985**, *4*, 1310−1312. (d) Erker, G.; Czisch, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059−2060. (e) Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. *Z. Naturforsch.* **1980**, *35b*, 1289−1297. (f) Scharf, W.; Neugebauer, D.; Schubert, U.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 601−602. (g) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 59−60. (h) Schumann, H.; Reier, F. W. *J. Organomet. Chem.* **1984**, *269*, 21−27. (i) See also citations in reference 6.

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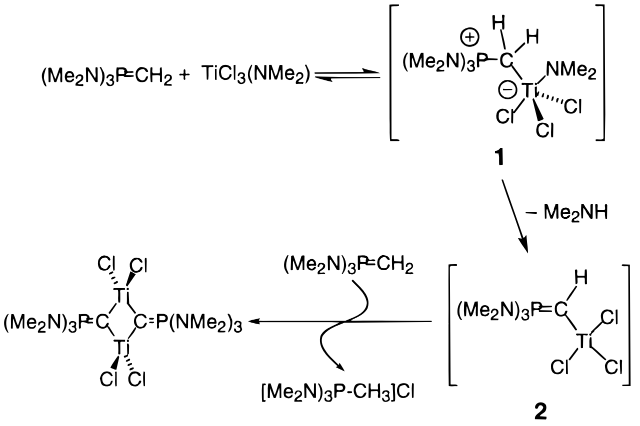
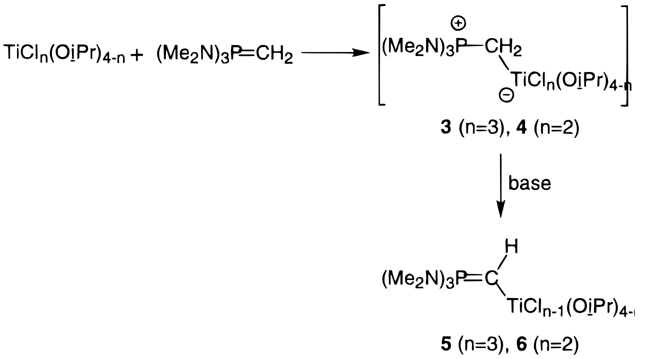
Scheme 1



Scheme 2



of Schmidbaur and co-workers, that reactions of phosphorus methylides with $Ti(NMe_2)_xCl_{4-x}$ ($x = 1, 2$) afford ylide-bridged metallacycles via action of the methylide as both nucleophile and base, and that these metallacycles also function as double oxophiles to give allenes from aldehydes.[6] We noted when preparing the metallacycles the loss of one dimethylamino group from each titanium center; that is, $Ti(NMe_2)Cl_3$, gave the metallacycle $[(Me_2N)_3P{=}CTiCl_2]_2$, in which no dimethylamino groups remain bound to Ti, and $Ti(NMe_2)_2Cl_2$ gave $[(Me_2N)_3P{=}CTiClNMe_2]_2$, in which each Ti bears one amide ligand. Scheme 1 shows the fundamental steps that are proposed to occur in this process. Interaction of the Lewis acidic Ti halide and nucleophilic ylide in adduct **1** activates both an ylide proton and a coordinated dimethylamino group to loss as dimethylamine. The resulting Ti-substituted ylide **2** may be deprotonated by base—in this case the phosphorus methylide—to give a complex with the composition of the observed metallacycle. The order of these steps may be reversed without changing the outcome. The intermediates are represented as monomers in Scheme 1 for simplicity; the mechanism probably involves dimeric or oligomeric Ti complexes at each stage.

When the relatively labile $TiNMe_2$ groups are replaced by Ti-alkoxides, the reaction takes a different course. Thus, the careful addition of $(Me_2N)_3P{=}CH_2$ to $TiCl_3O\textit{i}Pr$ in toluene solvent results in precipitation of the crystalline adduct **3**, analogous to **1**, in 77% yield (Scheme 2). The solid-state structure of **3**, determined by X-ray crystallography[55] and shown in Figure 1, is dimeric with bridging chloride ligands. The P–C(1) distance and $^1J_{PC}$ coupling constant, both characteristic of a P–C single bond, and the six-coordinate nature of the Ti centers verify the zwitterionic nature of the species in both the solid and solution phases. Adducts of this type have been previously observed.[7] As discussed in the preceding paper in this issue, the analogous complex **4**, prepared from $TiCl_2(OiPr)_2$ and $(Me_2N)_3P{=}CH_2$, offers significant advantages in subsequent olefination chemistry. However, **4** is much less stable than **3** and so must be used immediately after it is formed (*vide infra*). Adducts **3** and **4** may be deprotonated to give Ti-substituted ylides **5** and **6**, respectively (Scheme 2); $NaN(SiMe_3)_2$ is the most effective base we have tested in terms of convenience and selectivity for deprotonation vs Ti ligand substitution (see below). Note that ylides **5** and **6** resist elimination of alcohol analogous to the elimination of amine shown in Scheme 1, presumably because of the greater thermodynamic stability of Ti-alkoxides compared to Ti-amides.

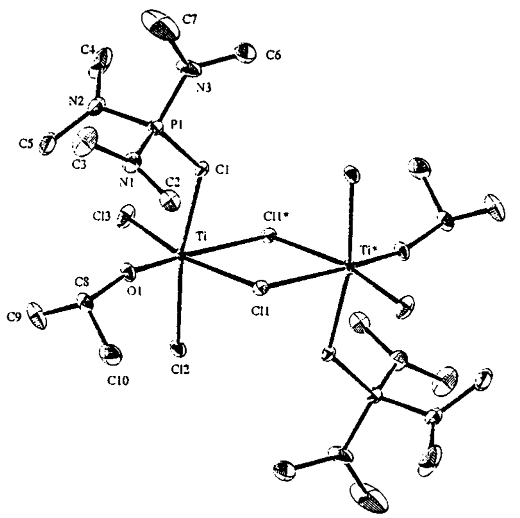


Figure 1. ORTEP diagram showing 30% probability thermal ellipsoids of $[(Me_2N)_3PCH_2TiCl_3O\textit{i}Pr]_2$, **3**. Pertinent bond lengths and angles: Ti–C1 2.217(5) Å, Ti–O1 1.722(4) Å, Ti–Cl1 2.445(2) Å, Ti–Cl1* 2.659(2) Å, Ti–Cl2 2.385(2) Å, Ti–Cl3 2.303(2) Å, P1–C1 1.743(5) Å; Ti–C1-P1 123.0(3)°, C1–Ti–Cl2 167.3(1)°, Ti–O1–C8 160.7(3)°.

When used in the one-pot double olefination process, **5** is generated in the presence of excess $NaN(SiMe_3)_2$. Preliminary results[1] had indicated that at least 4 equiv of $NaN(SiMe_3)_2$ and an excess of aldehyde were needed to obtain optimal yields of allenes. We believe that this is due primarily to the need for rapid deprotonation of a vinylphosphonium intermediate (*vide infra*) which can be achieved with the bulky bis(trimethylsilyl)amide base only at high concentration. The structure of the Ti-substituted ylide reagent under these conditions is therefore of interest. The use of excess base was found to produce several species, as follows.

^{31}P and ^{13}C NMR of reaction mixtures prepared with $(Me_2N)_3P{=}^{13}CH_2$ proved to be informative. The labeled carbon not only facilitates observation of the ylide and central allene carbon signals, but also allows for correlation of ^{31}P and ^{13}C NMR signals by comparison of their $^1J_{CP}$ coupling constants. The addition of 1.5 equiv of $NaN(SiMe_3)_2$ to a solution of **3** was shown to be sufficient for complete deprotonation of the adduct. However,

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[6] Hughes, K. A.; Dopico, P. G.; Sabat, M.; Finn, M. G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 554–555, and references therein.

[7] (a) Schmidbaur, H.; Scharf, W.; Fuller, H.-J. *Z. Naturforsch. B* **1977**, *32*, 858–862. (b) Fandos, R.; Gómez, M.; Royo, P.; García-Blanco, S.; Martínez-Carrera, S.; Sanz-Aparicio, J. *Organometallics* **1987**, *6*, 1581–1583. (c) Bestmann, H. J.; Arenz, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 559–560.

Table 1. Ylide ^{13}C NMR Resonances of Complex 3 in the Presence of $NaN(SiMe_3)_2$

equiv of $NaN(SiMe_3)_2$	^{13}C chemical shift (relative intensity)	$^1J_{PC}$, Hz	$^1J_{CH}$, Hz
1.5	175.8 (6)	100.4	
	129.1 (1)	102.8	
3	175.8 (8)	100.4	
	129.1 (1)	102.8	
	116.1 (2)	98.6	
4	175.8 (3)	100.4	123.3
	129.1 (1)	102.8	121.6
	116.1 (1)	98.6	117.9
4 (isolated, C_6D_6)	115.3	97.2	

mixtures of different titanated ylide species were observed in varying ratios depending on the equivalents of base added, as shown in Table 1. All the labeled carbon resonances observed possessed similar $^1J_{CP}$ and $^1J_{CH}$ coupling constants, ruling out direct interaction of $N(SiMe_3)_2$ with phosphorus or ylide carbon. The appearance of doublets of doublets in undecoupled ^{13}C NMR spectra indicated that all of these ylide carbon signals derived from CH groups. Upon addition of excess aldehyde to the sample containing 4 equiv of $NaN(SiMe_3)_2$, all of the ylide resonances in the mixture disappeared rapidly, and a clean allene signal was observed. Thus, each component of the Ti-substituted ylide mixture is either independently active in allene formation, or each is easily converted to an active species.

When 4 equiv of $NaN(SiMe_3)_2$ are used and the reaction mixture is subsequently evaporated, a viscous dark red oil, designated as complex **7**, is obtained. The ^{13}C NMR spectrum of a C_6D_6 solution of this species shows only one labeled resonance (last entry in Table 1). The ^1H NMR spectrum shows a doublet at 5.55 ppm ($^2J_{PH} = 6.0$ Hz), consistent with an olefinic proton, which correlates with the labeled ^{13}C resonance at 115.3 ppm (d, $^1J_{PC} = 97.2$ Hz) by $^{13}C-^1H$ HETCOR (Supporting Information) and DEPT analysis. The ^{31}P NMR spectrum shows a dominant peak at 56 ppm. These data are quite similar to those of the known[8] zirconium- and hafnium-substituted tris(dimethylamino) ylides **8** and **9** shown in Figure 2 and much different than those of ylide-bridged metallacycles such as **10**.[6,8a]

These data suggest that, in addition to deprotonating the ylide−Ti adduct, bis(trimethylsilyl)amide interacts with the Ti center and that ligand exchange rates of the various complexes are slow on the NMR timescale. Both ligand substitution (probably for chloride) and ligand association (to give anionic titanium centers) are possible. Note that the addition of more $NaN(SiMe_3)_2$ results in the formation of species bearing more upfield ylide resonances. Concentration of the reaction mixture apparently increases the amount of base coordinated to titanium, accounting for the predominance of the 115 ppm species in sample **7**.

$TiCl_2(OiPr)[N(SiMe_3)_2]$, prepared by the addition of 1 equiv of $NaN(SiMe_3)_2$ to $TiCl_3OiPr$, reacts with $(Me_2N)_3P{=}CH_2$, 3 equiv of $NaN(SiMe_3)_2$, and 4 equiv of 4-methylbenzaldehyde to give a 50% yield of 1,3-di-*p*-tolylallene.[1] In contrast, $TiCl(OiPr)[N(SiMe_3)_2]_2$, prepared by reaction of 2 equiv of $NaN(SiMe_3)_2$ with $TiCl_3OiPr$, does not react at all with $(Me_2N)_3P{=}CH_2$, the mixture showing only free methylide by ^{31}P and ^{13}C NMR. The addition of more

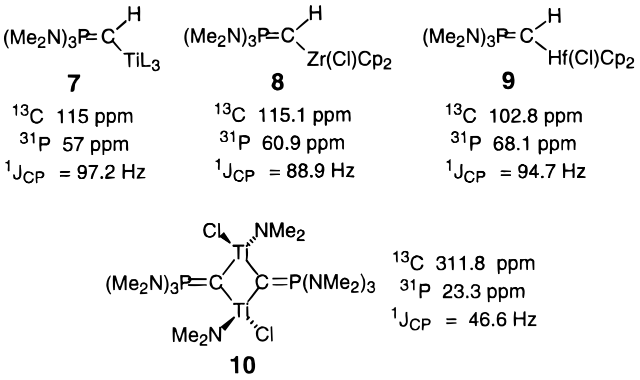
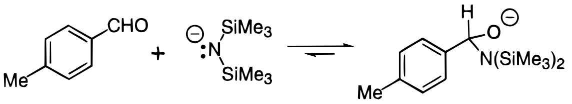


Figure 2. Summary of NMR Data for $(Me_2N)_3P{=}CH{-}ML_3$.

$NaN(SiMe_3)_2$ and aldehyde affords no allene in this case. Apparently, the bis(amido)titanium species is too hindered to interact with $(Me_2N)_3P{=}CH_2$, and the double olefination proceeds in the presence of excess base only when the base is added *after* the formation of the initial carbon−titanium bond.

Aldehyde Stoichiometry: Association with Bis(trimethylsilyl)amide. The reaction of varying equivalents of 4-methylbenzaldehyde with the mixture of reagents generated under standard "one-pot" conditions (complex **3** + 4 equiv $NaN(SiMe_3)_2$), was studied by ^{31}P and ^{13}C NMR spectroscopy. Rapid formation of diarylallene occurs upon addition of 4 equiv of *p*-tolualdehyde, but no change in the ylide species is observed over several hours when the ylide mixture is treated with only 2 equiv of aldehyde. However, ^{13}C NMR reveals a side reaction with the aldehyde in the latter case, causing disappearance of the carbonyl carbon peak at 190 ppm and the appearance of a new resonance at 167 ppm. When excess 4-methylbenzaldehyde is treated with $NaN(SiMe_3)_2$ in the absence of ylide reagent, the 167 ppm peak is observed along with unreacted aldehyde. These observations are consistent with the rapid formation of α-amino alkoxide species (eq 1), which have been previously characterized in the reactions of dialkylamide bases with aromatic aldehydes.[9]



(1)

To further investigate the observation that the first 2 equiv of aldehyde are made unavailable for reaction by complexation with base, a mixture of **3** and 4 equiv of $NaN(SiMe_3)_2$ was treated sequentially with 2 equiv of 4-methylbenzaldehyde followed by 2.5 equiv of *p*-anisaldehyde (Scheme 3). The dominant product of the reaction was the *p*-anisylallene, **11**, in spite of the substantially greater reactivity exhibited by 4-methylbenzaldehyde in a competition experiment.[1] When the reaction was performed by first adding 4 equiv of *p*-tolualdehyde followed by 8 equiv of *p*-anisaldehyde, **12** was the major product (Scheme 3). When 4 equiv of $NaN(SiMe_3)_2$ were pretreated with 8 equiv of *p*-tolualdehyde (converting the amide base to α-amino alkoxide), followed by the addition of 1 equiv of Ti-ylide adduct **3**, a typical yield of allene **12** was obtained. This demonstrates that the α-amino

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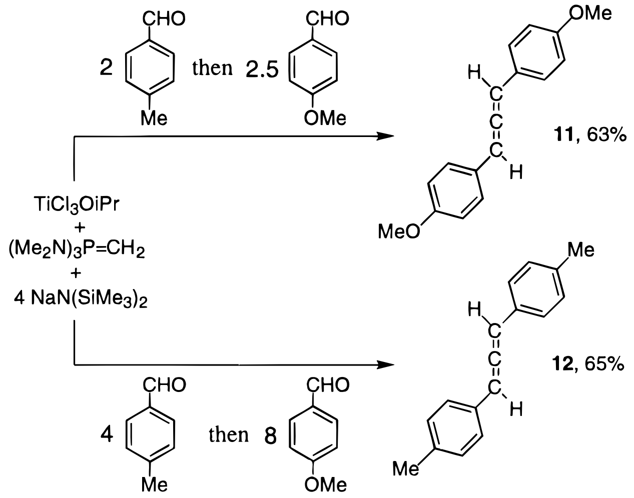
(8) (a) Schmidbaur, H.; Pichl, R.; Müller, G. *Chem. Ber.* **1987**, *120*, 39−44. (b) Schmidbaur, H.; Pichl, R.; Müller, G. *Chem. Ber.* **1987**, *120*, 789−794. (c) Schmidbaur, H.; Pichl, R. *Z. Naturforsch.* **1985**, *B40*, 352−356.

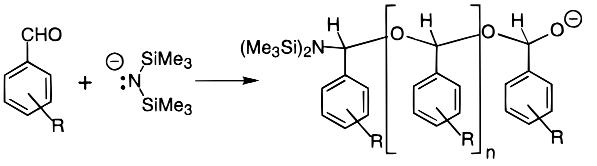
(9) (a) Comins, D. L.; Brown, J. D.; Mantlo, N. B. *Tetrahedron Lett.* **1982**, *23*, 3979−3982. (b) Comins, D. L.; Brown, J. D. *J. Org. Chem.* **1984**, *49*, 1078−1083.

Scheme 3



alkoxide mixture retains the Brønsted base activity required for both olefination steps (*vide infra*).

The extent of α-amino alkoxide formation was shown to depend upon the electrophilicity of the participating aldehyde and provides a rationale for the failure of the one-pot allene condensation process to accommodate electron-deficient substrates.[1] For example, the reaction of $NaN(SiMe_3)_2$ with a five-fold excess of *p*-bromobenzaldehyde leads to the conversion of nearly all the aldehyde to an α-amino alkoxide form. Thus, under the one-pot reaction conditions, electron-deficient aldehydes form α-amino alkoxide oligomers (eq 2), which renders them unreactive with metal-substituted ylide. Aqueous acidic workup of the reaction mixture regenerates the aldehydes, which therefore appear not to have been attacked, contrary to what would be expected for these substrates in the presence of a nucleophilic ylide.



(2)

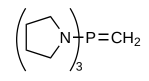
In order to block the association of bis(trimethylsilyl)amide with titanium, $TiCl_2(OiPr)_2$ (giving adduct **4**) was used in place of $TiCl_3OiPr$ (adduct **3**). When the one-pot double olefination reaction is performed with **4** and 2 or 3 equiv of $NaN(SiMe_3)_2$, allene **12** is isolated in 38% and 70% yields, respectively. These results are similar to the reactions of adduct **3** and 3 or 4 equiv of $NaN(SiMe_3)_2$, respectively; note that no allene is produced using adduct **3** and 2 equiv of base. Therefore, the ylide complex **6** produced from **4** (Scheme 2) does indeed participate to a lesser extent in ligand exchange reactions with bis(trimethylsilyl)amide. Presumably, the presence of two isopropoxide groups on titanium renders the metal center more hindered, less electrophilic, and less apt to substitute chloride than the monoisopropoxide species **5**.

Variation of Ylide and Metal Halide Components. Various metal halide reagents were screened for activity in the double olefination process with $(Me_2N)_3P{=}CH_2$ under standard conditions using 4-methylbenzaldehyde (Table 2). Titanium chloroalkoxy species (entries 1−6, 9) proved to be the most successful. $ZrCl_4$, $HfCl_4$, and $TiCl_2(OiPr)_2$ were also tested with less reactive substrates such as 4-chlorobenzaldehyde, 2-furaldehyde, and benzophenone, but the yields of allenes from these substrates remained poor.

Table 2. Metal Halide Components Tested for One-Pot Double Olefination Activity

entry	metal halide	% yield of allene **12**
1	$Ti(III)Cl_3{\cdot}(THF)_3$	58
2	$TiCl_3OiPr$	56
3	$TiCl_2(OiPr)_2$	70
4	$TiCl(OiPr)_3$	trace
5	$TiCl_3[OCH(CF_3)_2]$	50
6	$TiCl_3OtBu$	54
7	$TiCl_2OiPr[N(SiMe_3)_2]$	50
8	$TiCl_4$	none
9	$TiBr_3(OiPr)$	14
10	$TiCl_3(O$-2,6-$Me_2Ph)$	42
11	Cp_2TiCl_2	trace
12	Cp_2TiCl_3	3(allene), 8(styrene)
13	$HfCl_4$	32
14	$ZrCl_4$	40
15	$SnEt_3Cl$	1
16	$SnPh_3Cl_3$	21
17	$SiMe_3Cl$	9(allene), 6(styrene)
18	$SiMe_2Cl_2$	none
19	(catechol)BCl	2

Table 3. Phosphorus Compounds Screened for One-Pot Double Olefination Activity

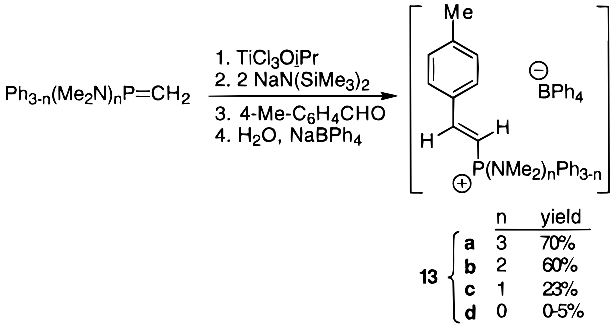
entry	phosphorus methylide	yield of allene **12**
1	$Me_3P{=}CH_2$[a]	trace
2		none
3	$(4\text{-OMe-Ph})_3P{=}CH_2$	none
4	$(2,4,6,\text{-(OMe)}_3\text{-Ph})_3P{=}CH_2$	none
5	$(4\text{-NMe}_2\text{-Ph})_3P{=}CH_2$	9% + olefin
6	$(MeO)_2P(O)CH_2^-$	none
7	$(nBu)_3P{=}CH_2$	none
8	$(Ph)_3P{=}CH_2$	trace with $TiCl_3OiPr$ none with $TiCl_4$
9	$(Ph)_2(Me_2N)P{=}CH_2$[a]	32% with $TiCl_3OiPr$ 27% with $TiCl_4$
10	$(Ph)_2(Me_2N)P{=}CH_2$[a]	62%
11	$(Me_2N)_3P{=}CH_2$[a]	56% with $TiCl_3OiPr$ 70% with $TiCl_2OiPr_2$

[a] Isolated, purified methylides were used; otherwise, ylides were generated *in situ* from the corresponding phosphonium salt and $NaN(SiMe_3)_2$ (except for entry 6, for which NaH was employed).

A variety of phosphorus ylides were also tested for reactivity with 1 equiv of $TiCl_3OiPr$, 4 equiv of $NaN(SiMe_3)_2$, and 8 equiv (except where noted) of 4-methylbenzaldehyde (Table 3). Only the dimethylamino-substituted ylides showed substantial allene yields. The methylides $Ph_3P{=}CH_2$ and $Ph_2(Me_2N)P{=}CH_2$ were also tested with $TiCl_4$ to probe the response of the reaction to a change in metal halide structure. As discussed below, the results show that dialkylamino-substituted phosphorus components are required, presumably because of their electron-rich nature, but that the more electrophilic $TiCl_4$ does not enhance the reaction relative to $TiCl_3(OiPr)$.

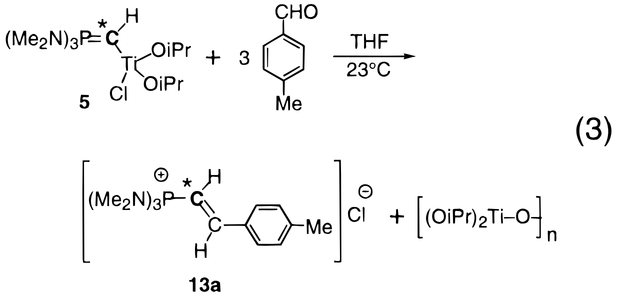
Stepwise Condensation of Aldehydes to Allenes.[1a] *Preliminary NMR Observations.* With the use of fully labeled $(Me_2N)_3P{=}^{13}CH_2$, we were able to analyze reaction mixtures by ^{13}C and ^{31}P NMR under standard reaction conditions in nondeuterated solvents. Accordingly, the one-pot titanium-substituted ylide reagent was generated by the reaction of $(Me_2N)_3P{=}^{13}CH_2$ and $TiCl_3OiPr$ in THF, followed by the addition of 4 equiv of $NaN(SiMe_3)_2$. Upon addition of 4 equiv of 4-methylbenzaldehyde, the peaks of two intermediate species ap-

Scheme 4



peared (spectra included in Supporting Information): ^{31}P, 52 ppm; ^{13}C, 105 ppm (doublets, $^1J_{PC}$ = 164 Hz); and at ^{31}P, −18 ppm; ^{13}C, 158 ppm (doublets, $^1J_{PC}$ = 156 Hz). The former set of signals is identical to those of vinylphosphonium salt **13a** (shown below; this is compound **3a** in the preceding paper). Repetition of this experiment at variable temperature (−40 °C to 25 °C) showed the latter species (^{31}P, −18 ppm; ^{13}C, 158 ppm) to be derived from the vinylphosphonium compound and to be the immediate precursor of HMPA and allene. The upfield nature of the ^{31}P NMR resonance is consistent with a five-coordinate phosphorus species, such as an oxaphosphetane.[10,11] Thus, the one-pot double olefination process proceeds by formation and subsequent deprotonation of vinylphosphonium species. These steps were investigated separately, as discussed below.

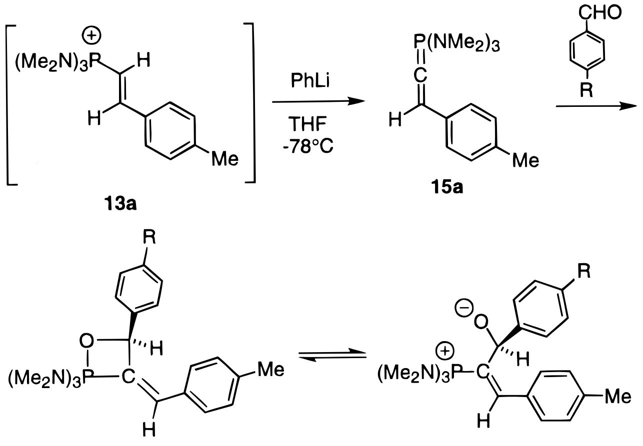
Step 1: Formation of Vinylphosphonium Salts. The reaction of titanium-substituted ylides **5** or **6** with aromatic aldehydes affords vinylphosphonium salts with no observable intermediate (eq 3). Thus, when ^{13}C-labeled **5** is treated with 4-methylbenzaldehyde at −55 °C in THF and examined by ^{31}P and ^{13}C NMR at low temperature, only ^{13}C-labeled **13a** is detected.



(3)

The response of the vinylphosphonium-forming step to changes in ylide nucleophilicity was probed with a series of (aryl)(dimethylamido)phosphorus methylides (Scheme 4). Mirroring the results of one-pot allene formation noted above (Table 3), vinylphosphonium salts **13** are isolated with the BPh_4^- counterion in yields directly proportional to the number of NMe_2 groups on phosphorus.

Scheme 5



16a R = 4-Me
16b R = 4-OMe
16c R = 3,4,5-(OMe)3

17a R = 4-Me
17b R = 4-OMe

Step 2: Generation and Trapping of Allenic Phosphoranes. The reaction of purified vinylphosphonium salt **13a**·BPh$_4$ with NaN(SiMe$_3$)$_2$ and 4-methylbenzaldehyde provides allene **12** in only 20% yield, whereas the same allene is produced by a one-pot condensation using NaN(SiMe$_3$)$_2$ in 70% yield. Variations in temperature, the order of addition of aldehyde and base, and time elapsed between addition of base and addition of aldehyde produced little improvement. The most successful reaction using NaN(SiMe$_3$)$_2$ (26% yield) occurs at room temperature with simultaneous addition of the trapping aldehyde and the base aldehyde, the conditions closest to those of the one-pot double olefination. Conversely, the longer the vinylphosphonium salt is allowed to react with the base prior to the addition of the aldehyde, the poorer is the allene yield. Many of these reaction mixtures, particularly those conducted at room temperature, show complex ^{31}P NMR spectra with several peaks in the 55−65 ppm range, suggesting that a variety of four-coordinate phosphorus side products are produced. A plausible side reaction is polymerization of the vinylphosphonium species, in a cascade mechanism reminiscent of Posner's Michael−Michael ring closure synthesis of cyclic phosphonates.[12] A similar polymerization side reaction with a vinylphosphonium salt in the synthesis of an allylamine has been reported.[13] As described in the accompanying paper, PhLi was found to be an efficient base for the deprotonation of isolated vinylphosphonium salts.

Based on its subsequent reactivity, the conjugate base of **13a** is likely to have the allenic phosphorane/ylide structure **15a** (see below, Scheme 5). The diminished basicity of **15a** relative to bis(trimethylsilyl)amide allows for some extention of the reaction scope, as described for cyclohexanecarboxaldehyde in eqs 2 and 3 of the preceding paper. Wittig reactivity of allenic phosphorane **15a** is not general with aliphatic aldehydes, however, and appears to be bracketed by steric effects: the bulkier substrate pivalaldehyde does not react with **15a**, while less hindered aldehydes (*n*-hexanal and **14**) are deprotonated by **15a**. The latter process was observed to be rapid at −65 °C by ^{31}P and ^{13}C NMR, showing immediate conversion of **15a** back to vinylphosphonium salt **13a**

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[10] Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 2823−2831.

[11] (a) Vedejs, E.; Marth, C. F. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH: New York, 1994; pp 297−313. (b) Gorenstein, D. G., Ed. *Phosphorus-31 NMR: Principles and Applications*; Academic Press: Orlando, FL, 1984. (c) Grim, S. O. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; Chapter 18, pp 645−664. (d) Grayson, M.; Griffith, E. J., Eds. *Topics in Phosphorus Chemistry, Vol. 5, P-31 Nuclear Magnetic Resonance;* John Wiley and Sons, Inc.: New York, 1967.

[12] Posner, G. H.; Lu, B. S. *J. Am. Chem. Soc.* **1985,** *107*, 1424−1426.

[13] Meyers, A. I.; Lawson, J. P.; Carver, D. R. *J. Org. Chem.* **1981**, *46*, 3119−3123.

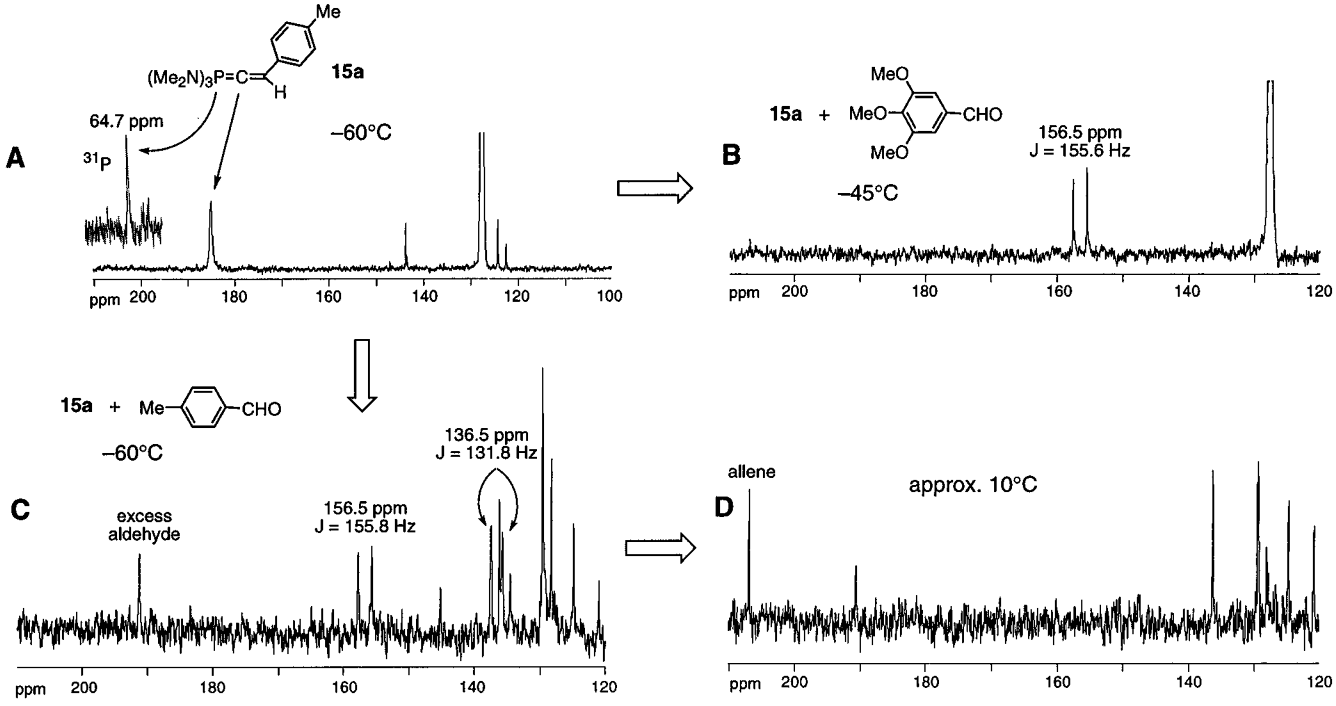
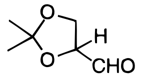


Figure 3. NMR spectra showing the generation and trapping of allenic phosphorane **15a**-$^{13}C_1$.

upon addition of the aldehyde. Ketones such as fluorenone, benzophenone, and acetophenone were also ineffective trapping agents for allenic phosphorane **15a**. This parallels the reactivity of several types of less nucleophilic stabilized ylides that have been shown to react with aldehydes in preference to ketones, presumably due to steric factors.[14]



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Characterization of Reaction Intermediates. When ^{13}C labeled **13a**·BPh_4 in THF is treated with phenyllithium at −65 °C, the ^{31}P and ^{13}C (C1) NMR signals at 52.0 and 106.3 ppm, respectively ($^1J_{PC}$ = 166.7 Hz), immediately disappear in favor of broad peaks appearing at 65 ppm (^{31}P) and 185 ppm (^{13}C), without discernable $^{31}P-^{13}C$ splitting (Scheme 5, Figure 3A).[15] Decreasing the temperature from −65° to −85 °C provided somewhat sharper peaks but no splitting. These resonances are assigned to the allenic phosphorane **15a** derived from deprotonation at C1.[16]

Intermediate **15a** is stable for at least 4 h at −65 °C as monitored by NMR (decomposing above −30 °C to uncharacterized products) and proved to be an active olefinating reagent. Figures 3−5 show ^{13}C spectral changes in the 120−210 ppm region (containing all resonances showing one-bond P−C coupling except for residual vinylphosphonium salt at 105 ppm) of reactions of **15a** with various aldehydes as a function of temperature. Figures 6 and 7 show ^{31}P NMR spectra of some of the same mixtures. Chemical shifts and observed coupling constants of important resonances are shown and are also collected in Table 4. The use of phosphorus methylide that is completely ^{13}C-labeled at the ylide carbon allows for the positive identification in the ^{31}P NMR of species retaining the P−C bond. These data provide a nearly complete picture of intermediate species present during the second, allene-forming, olefination event.

Thus, the addition of 3,4,5-trimethoxybenzaldehyde to **15a**-$^{13}C_1$ in THF at −65 °C results in immediate and clean conversion to a species displaying a single new labeled ^{13}C NMR resonance at approximately 156 ppm with a large $^1J_{CP}$ coupling constant (Figure 3B). Similar species are formed upon the addition of 4-methylbenzaldehyde (Figure 3C) and 4-methoxybenzaldehyde (Figure 5A) to **15a** at low temperature. Signals with corresponding $^1J_{CP}$ coupling constants are found in the ^{31}P NMR spectra at approximately −21 ppm (Figures 6A and 7A). These resonances are assigned to the oxaphosphetane structures **16a-c** (Scheme 5), on the basis of the characteristic[10,11,17] upfield ^{31}P chemical shift[18] and match those of intermediates observed in the NMR of one-pot allene condensation reactions at 25 °C. Note that both ^{13}C and ^{31}P resonances for oxaphosphetane **16b** (spectra 5A and 7A) are broadened when compared to those for oxaphosphetane **16a** (spectra 4A and 6A).

When excess aldehyde is used to trap the allenic phosphorane, a second set of signals often appears at approximately 137 ppm for ^{13}C and 60 ppm for ^{31}P, with smaller $^1J_{CP}$ of about 130 Hz, as shown for the reactions of **15a** with 4-methylbenzaldehyde and 4-methoxybenzaldehyde (Figures 3C, 4A, and 5A). The ratio of the two species in each case changes with concentration and the nature of the trapping aldehyde; occasionally, only the second set of resonances appears. The second species is

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[14] March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley and Sons, Inc.: New York, 1985; p 846 and references therein.

[15] Peak width at half-height for the ^{13}C signal is approximately 50 Hz; thus the $^{13}C-^{31}P$ coupling constant must be small or the compound is undergoing a conformational equilibrium. In one instance, a poorly resolved ^{13}C doublet was observed with a splitting of 18 Hz.

[16] For a related deprotonation reaction, see: Stang, P. J.; Arif, A. M.; Zhdankin, V. V. *Tetrahedron* **1991**, *47*, 4539−4546.

[17] Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863−927.

[18] The analogous oxaphosphetane **16c** prepared with 3,4,5-trimethoxybenzaldehyde shows the ^{13}C ylide resonance at 156.5 ppm, with $^1J_{CP}$ = 157.4 Hz.

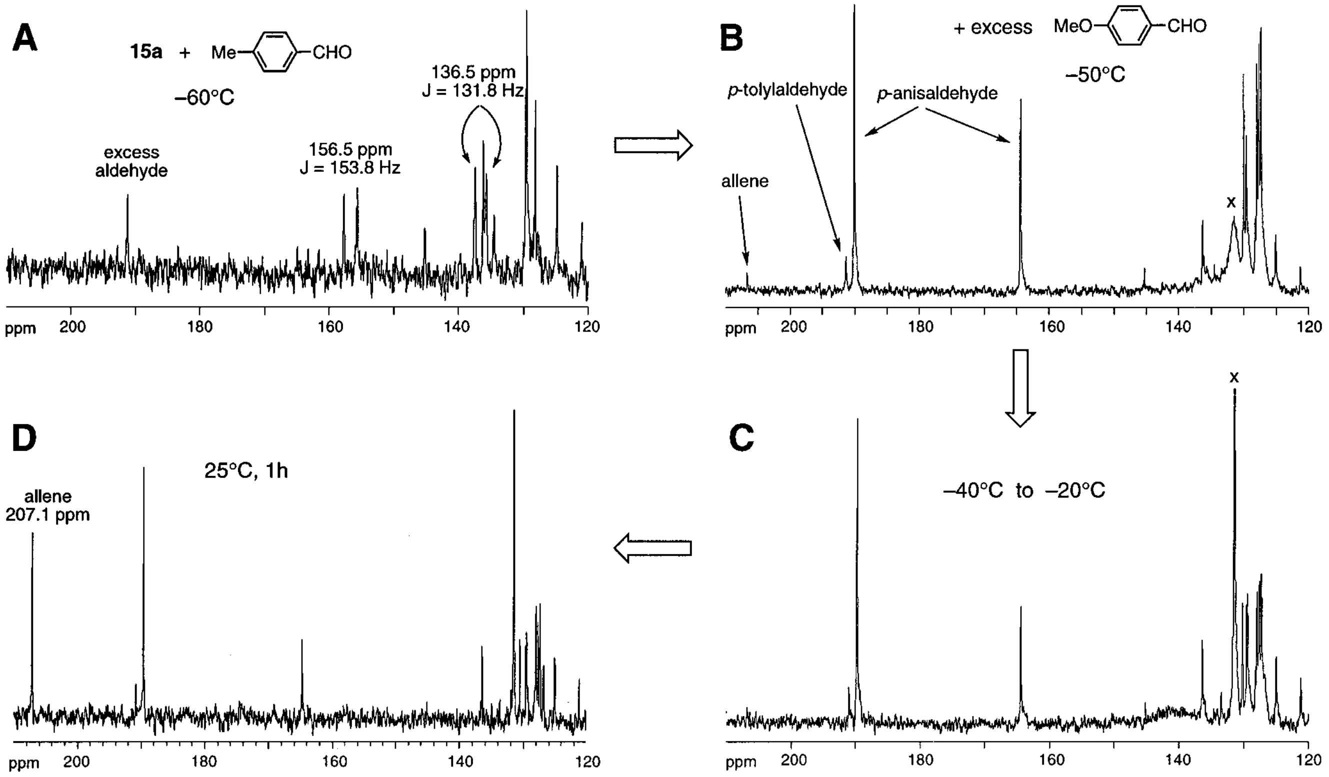

Figure 4. ^{13}C NMR spectra showing the generation and reaction of oxaphosphetane/betaine **16a**/**17a**.

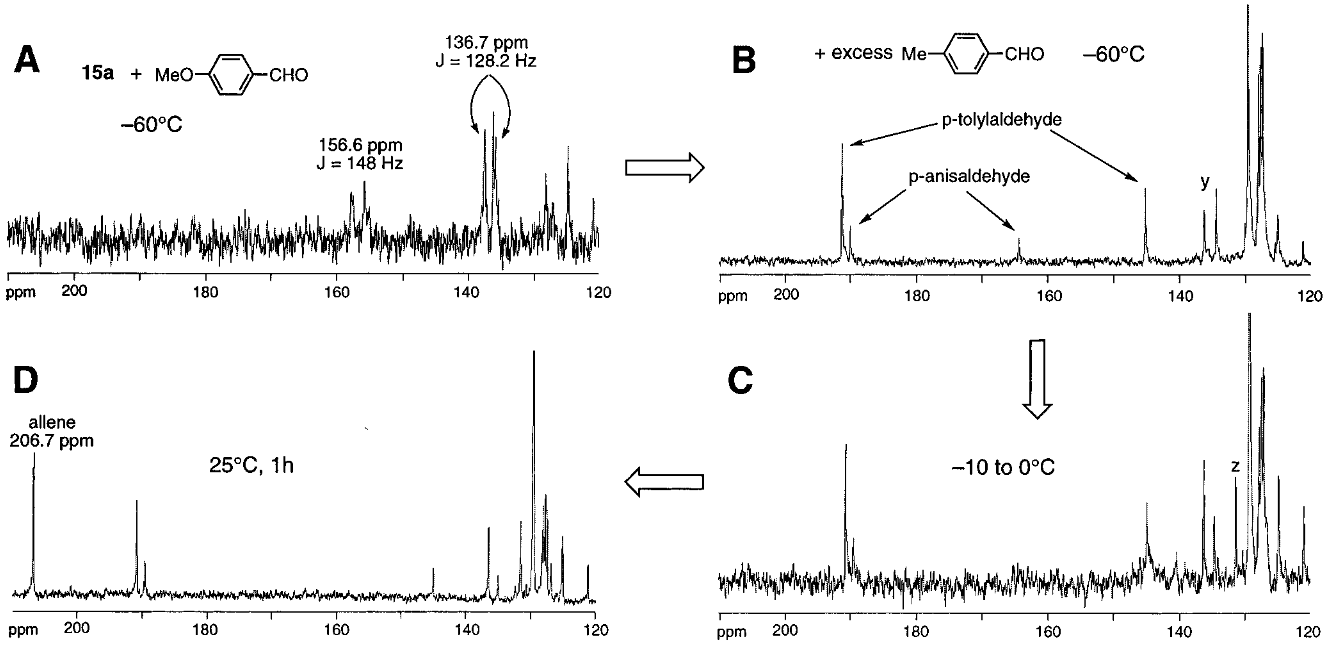

Figure 5. ^{13}C NMR spectra showing the generation and reaction of oxaphosphetane/betaine **16b**/**17b**.

proposed to be the β-oxidovinylphosphonium (betaine) **17a** on the basis of the downfield ^{31}P chemical shift and its subsequent reactivity (see below). The presence of lithium salts has long been known to promote betaine formation, and the oxaphosphetane form is presumed to precede the appearance of the betaine in analogy to standard Wittig processes.[17]

Warming a sample containing a mixture of **16a** and **17a** to room temperature in the NMR probe causes the two ^{13}C doublets to disappear and an allene singlet to emerge at about 207 ppm (Figure 3D). Interestingly, in this and all other cases investigated by variable-temperature NMR, the appearance of the characteristic ^{13}C signal for allene (central carbon at 206–208 ppm) and ^{31}P signal for HMPA (26 ppm) is not simultaneous with the disappearance of the precursor resonances. Instead, all ^{13}C and ^{31}P doublets disappear until a temperature of approximately 0 °C is reached, whereupon the allene ^{13}C signal begins to grow; HMPA does not appear in the ^{31}P NMR until sample temperatures approach 20 °C. This variable-temperature NMR behavior is consistent in the spectra of all cases investigated, but the temperatures at which changes occur vary from case to case. In all cases, a temperature range is observed in which no ^{31}P or labeled ^{13}C resonances are visible. For example, Figure 6B shows the ^{31}P signals for a mixture of **16a** and

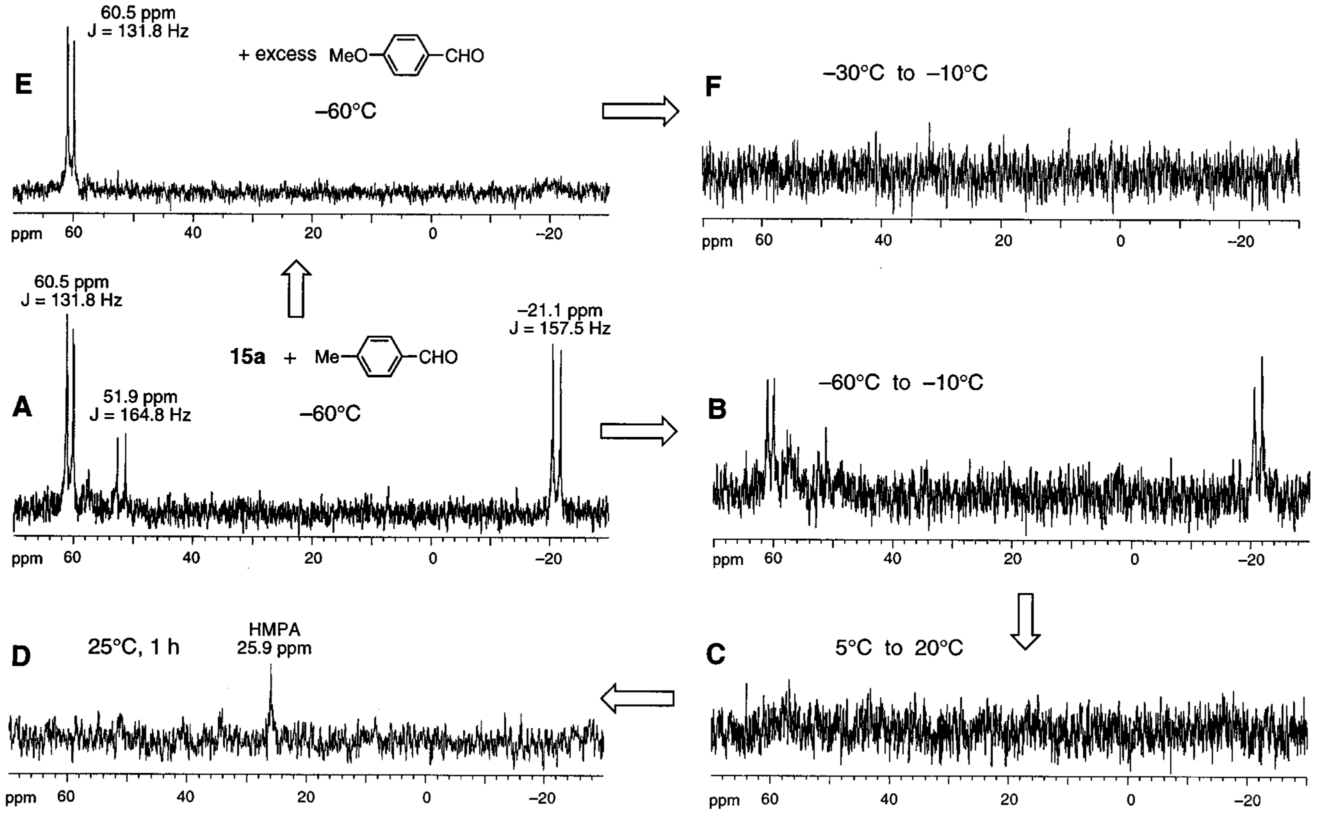

Figure 6. ^{31}P NMR spectra showing the generation and reaction of oxaphosphetane/betaine **16a**/**17a**.

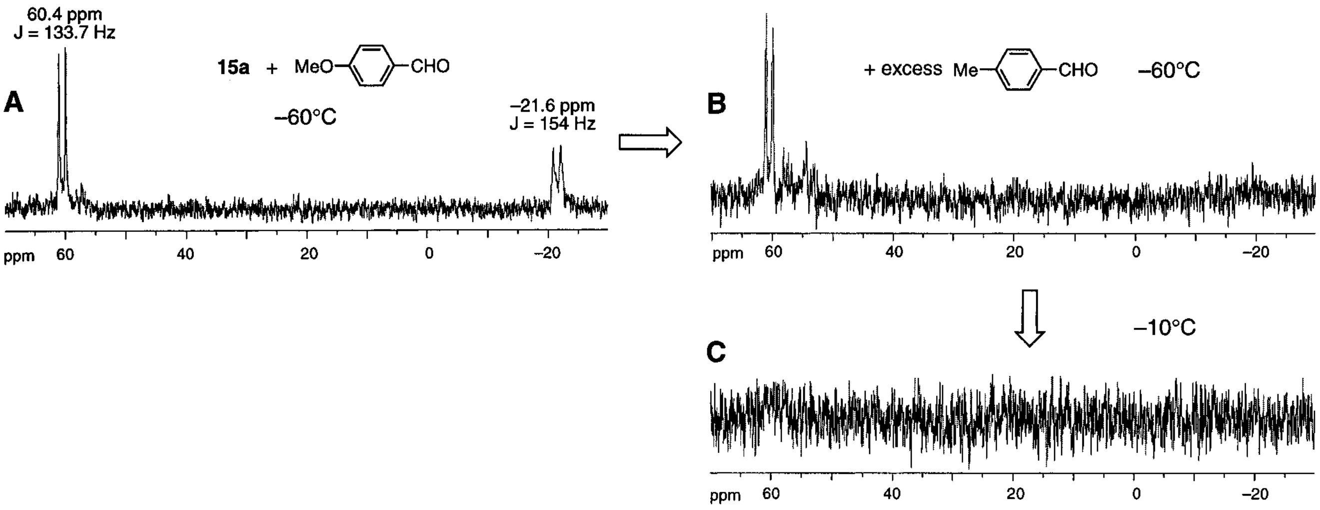

Figure 7. ^{31}P NMR spectra showing the generation and reaction of oxaphosphetane/betaine **16b**/**17b**.

Table 4. ^{13}C and ^{31}P Resonances of Species Derived from 13a·BPh$_4$-^{13}C$_1$

figure	assignment	^{13}C signal (ppm)	^{31}P signal (ppm)	$^{1}J_{CP}$ (obsd)
3A	**15a**	184.5	64.7	not obsd
3C	**16a**	156.5		155.8
6A	**16a**		−21.1	157.5
3C	**17a**	136.5		131.8
6A	**17a**		60.5	131.8
5A	**16b**	156.6		148 (br)
7A	**16b**		−21.6	154 (br)
5A	**17b**	136.7		128.2
7A	**17b**		60.4	133.7
3B	**16c**	156.5		155.6

17a to undergo some line broadening and begin to disappear as temperature is raised from −60 °C. As the NMR probe reaches a temperature of 5−20 °C, all signals are gone (Figure 6C), and the singlet for HMPA does not appear until the sample is allowed to stand at 25 °C for 1 h (Figure 6D).[19]

Additional data was obtained by the treatment of oxaphosphetanes generated *in situ* from one aldehyde with an excess of a different aldehyde. As shown by

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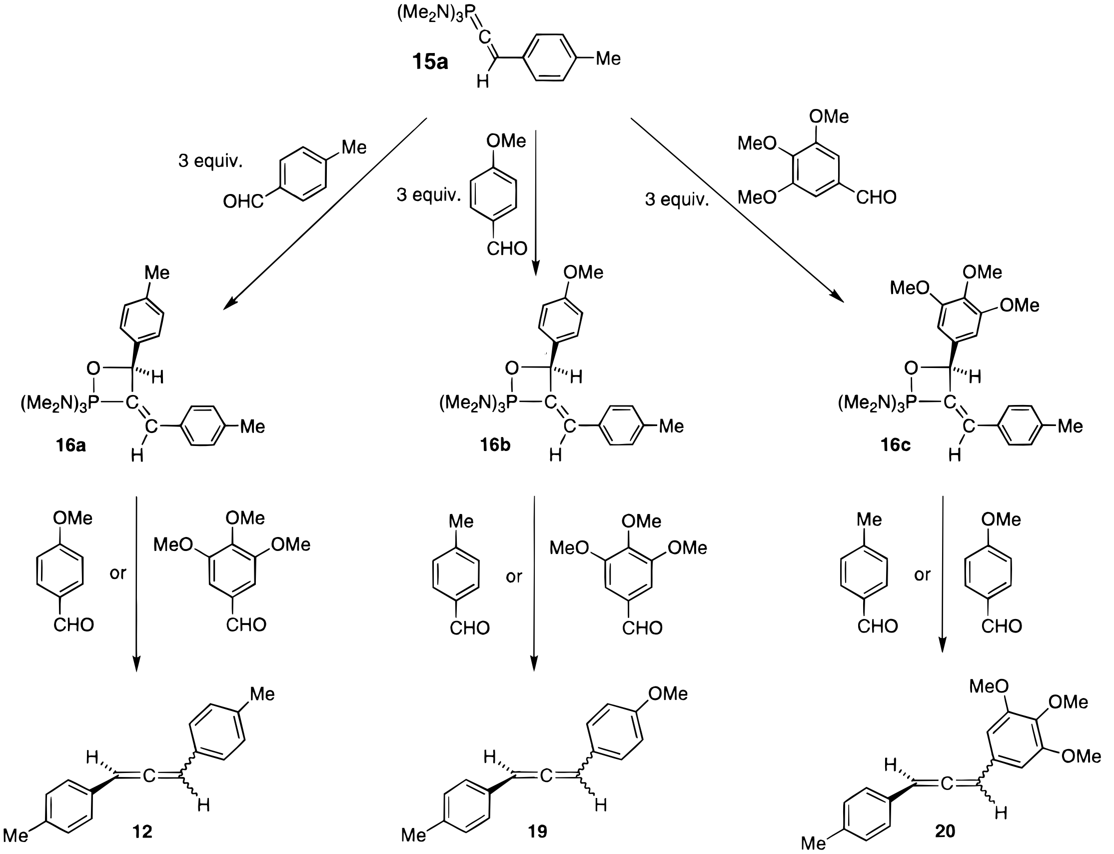
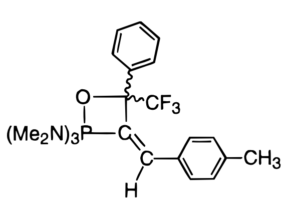
[19] The third ^{31}P doublet (51.9 ppm) as shown in Figure 6A is from residual vinylphosphonium salt **13a**, from which **16a** is derived. The presence of **13a** in these NMR samples is not unexpected, since it is not completely soluble in THF at low temperature at concentrations used for NMR investigation, and thus small amounts can escape reaction with PhLi. After excess PhLi is quenched by the addition of aldehyde, some of the remaining **13a** may dissolve and thus be detected in the NMR. When care is taken to dissolve **13a** as much as possible before PhLi addition, both ^{13}C and ^{31}P resonances for this species are diminished. Interestingly, while the ^{13}C signal for this species remains unchanged upon warming as would be expected for a vinylphosphonium cation, the ^{31}P resonance disappears along with the others.

Scheme 6



Figures 4B, 5B, 6E, and 7B, both ^{13}C and ^{31}P resonances for oxaphosphetanes **16a** and **16b** disappear immediately upon addition of excess aldehyde at low temperature. The ^{31}P resonances for the putative betaines **17a** and **17b** remain (Figures 6E and 7B), but the corresponding ^{13}C peaks are not similarly clear. In each case, the original doublet signal assigned to betaine disappears upon addition of excess aldehyde, but new peaks arise that may correspond to this species. For betaine **17a**, spectrum 4B shows a new broad singlet (marked “x”) appearing at 131.5 ppm, which sharpens as the sample temperature is raised (Figure 4C). Three small singlets (marked “y” and “z”) appear upon addition of excess *p*--tolualdehyde to **16b/17b** (Figures 5B and 5C). Different allenes are isolated in ≥70% yield from each reaction (Figures 4D and 5D), incorporating only the first aldehyde added to allenic phosphorane **15a** (see below).

The oxaphosphetane **18**, formed from the reaction of **13a**·BPh_4 with PhLi followed by trifluoroacetophenone, is stable at room temperature (^{31}P NMR −22 ppm; ^{13}C NMR 150.1 at −50 °C, 151.9 at 20 °C; $^{1}J_{CP} = 170.3$ Hz), decomposing only when heated to 50 °C.



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In order to further investigate the potential reversibility of the transformation of allenic phosphorane to oxaphosphetane, ^{13}C-labeled species **16a**, **16b**, and **16c** were generated from a single sample of **15a**-$^{13}C_1$ and 6 equiv of three different aldehydes at −50 °C. Each oxaphosphetane sample was divided into two parts, and treated at −50 °C with 20 equiv of each of the remaining two aldehydes, and then allowed to warm to room temperature. In each case, reversible dissociation of oxaphosphetane into allenic phosphorane and aldehyde would result in the production of two allenes, with predominant incorporation of the aldehyde present in greater excess. Examination of the crude reaction mixtures by ^{13}C NMR showed each of the aldehyde carbonyl and central allene carbon resonances to be well resolved and revealed that only the allene deriving from the initially-formed oxaphosphetane was produced (Scheme 6; for simplicity, betaine isomers are not shown).

Asymmetric Induction in Allene Formation. Chiral auxiliaries were used on both titanium and phosphorus to probe the reaction mechanism. The large molar optical rotations of 1,3-diarylallenes ($[\Phi]^{25}_{D} > 1900$)[20] allow for the reliable detection of small degrees of enantiomeric enrichment. Consistent with the elimination of titanium oxide prior to the allene−forming step, the use of $TiCl_3$-(*O*-menthyl) (where *O*-menthyl is the alkoxide derived from (+)-menthol) in place of $TiCl_3OiPr$ in the one-pot procedure with 4-methylbenzaldehyde affords the corresponding allene as a racemate in 60% yield.

Aryl phosphorus methyl phosphonium salts **21** and **22**, bearing chiral ether moieties *ortho* to phosphorus, provided allene **23** by the one-pot condensation with benzaldehyde in 5−11% enantiomeric excess in the *R*-isomer shown (Scheme 7).[21] The corresponding reaction of **22**

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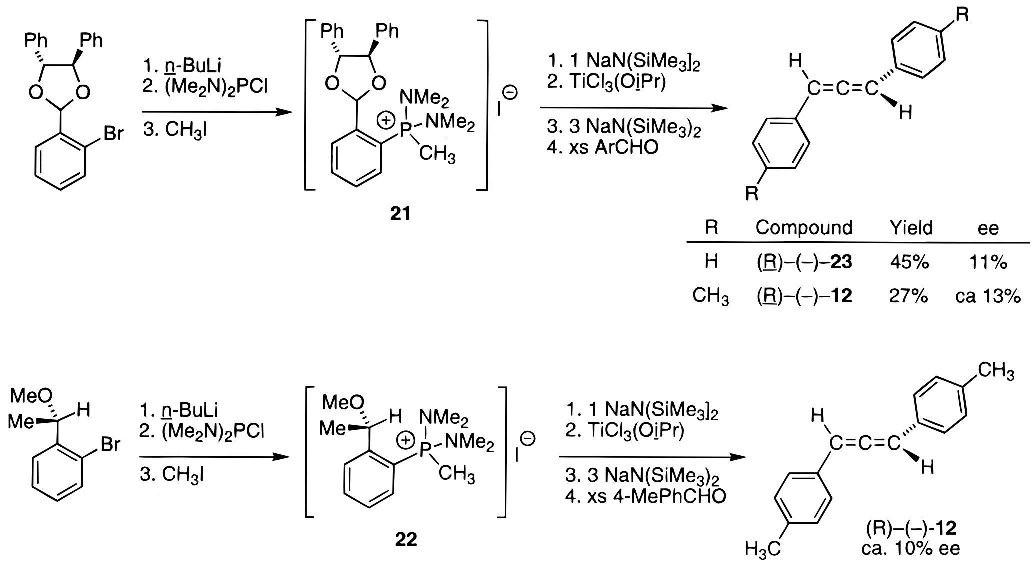
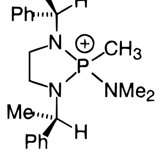
(20) (a) Ruch, E.; Runge, W.; Kresze, G. *Angew., Chem. Int. Ed. Engl.* **1973**, *12*, 20−25. (b) Runge, W.; Kresze, G. *J. Am. Chem. Soc.* **1977**, *99*, 5597−5603. (c) Brewster, J. H. In *Topics in Stereochemistry, Volume 2*; Allinger, N. L., Eliel, E. L., Eds.; Wiley-Interscience Publishers: New York, 1967.

Scheme 7



R	Compound	Yield	ee
H	(R)-(–)-**23**	45%	11%
CH_3	(R)-(–)-**12**	27%	ca 13%

with 4-methylbenzaldehyde gave allene **12** with a similar optical rotation as **23** and therefore presumably a similar enantiomeric excess. Enantiomerically pure methylphosphonium **24** was also prepared, but gave no allene under standard one-pot conditions, possibly due to its increased steric demand around the phosphorus center relative to the $(Me_2N)_3P$ unit.



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Diastereomeric Induction Using Chiral Aldehydes. Transfer of asymmetry from chiral aldehydes has previously been observed in the Wittig reaction.[22] Aldehydes **25**–**27** were employed as equimolar trapping agents for the allenic phosphorane **15a** derived from $[(Me_2N)_3P^{13}CH{=}CHC_6H_4CH_3]BPh_4$, and the resulting diastereomeric oxaphosphetanes were observed by ^{13}C NMR at −60 °C. Figure 8 and Schemes 8 and 9 show the results along with those of 4-methylbenzaldehyde for comparison: in each case, an oxaphosphetane intermediate analogous to **16** was immediately generated, and no betaine isomers were observed. The species derived from the achiral aldehyde shows a single doublet arising from the $^1J_{CP}$ interaction with the adjacent phosphorus center whereas each of the chiral substrates produces an intermediate composed of two isomers, revealed by the appearance of two sets of doublets.

The diastereomeric ratios of these oxaphosphetanes may be compared to the ratio of allenes produced by allowing the samples to warm to room temperature. Thus, aldehyde (±)-**25** gives rise to oxaphosphetane structure **28** in a 1:1 diastereomeric ratio, but diastereomers of allene **30** are formed in a ratio of 2.5:1 (Scheme 8, top). The same allene prepared in the opposite order—that is, by incorporating aldehyde **25** into a vinylphosphonium salt (**29**)—is formed in a 1:1 diastereomeric ratio (Scheme 8, bottom). When substrate **26** is employed as a trapping aldehyde for **15a**, the diastereomeric ratio of oxaphosphetanes (1:1) matches that of allene **31** produced (Scheme 9). Aldehyde **27**, derived from (*R*,*R*)-stilbene diol, shows a ratio of intermediates of approximately 2.5:1, but diastereomeric allenes **32** are formed as a 1.7:1 mixture (Scheme 9).

Discussion

The one-pot conversion of aromatic aldehydes to allenes by titanium-substituted ylides is shown to proceed in three steps: synthesis of vinylphosphonium salts by elimination of titanium oxides, vinylphosphonium deprotonation, and condensation of the resulting allenic phosphorane with another aldehyde. An investigation of the composition of the ylide species under the one-pot conditions reveals a family of complexes differing by titanium ligand substitution, and also a process of association between aldehyde and base that removes some aldehydes from the desired reaction pathway.

The precise composition of the various ylide complexes present under the one-pot double olefination conditions cannot be firmly established from the available NMR data (Table 1). A working hypothesis is that the resonances at 175, 129, and 116 ppm correspond to 0 [$(Me_2N)_3P{=}CHTi(Cl)_2(O\textit{i}Pr)$, complex **5**], 1 [$(Me_2N)_3P{=}CHTi(Cl)(O\textit{i}Pr)(N(SiMe_3)_2)$, complex **33**], and 2 [$(Me_2N)_3P{=}CHTi(Cl)(O\textit{i}Pr)(N(SiMe_3)_2)_2^-$, complex **34**] equivalents of bis(trimethylsilyl)amide ligands on titanium, respectively. It would be expected that the electron-donating effects of the amide group would result in an upfield shift of the resonance of the attached ylide carbon. The nonincorporation of the first 2 equiv of aldehyde in the

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(21) For use of chiral ylides in the synthesis of enantiomerically enriched alkenes, see: (a) Hanessian, S.; Gomtsyan, A.; Payne, A.; Herve, Y.; Beaudoin, S. *J. Org. Chem.* **1993**, *58*, 5032–5034. (b) Denmark, S. E.; Chen, C.-T. *J. Am. Chem. Soc.* **1992**, *114*, 10674–10676. (c) Hanessian, S.; Delorme, D.; Beaudoin, S.; Leblanc, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5754–5756. (d) Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 5699–5700. (e) Bestmann, H. J.; Lienert, J. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 763–764. (f) Tömösközi, I.; Janzso, G. *Chem. Ind. (London)* **1962**, 2085–2086. (g) In a related reaction, optically active allenes were prepared using an ylide bearing a menthol substituent at the ylide carbon: Tömösközi, I.; Bestmann, H. J. *Tetrahedron Lett.* **1964**, *20*, 1293–1295. (h) See also: Stang, P. J.; Learned, A. E. *J. Org. Chem.* **1989**, *54*, 1779–1781. (i) For enantioselective Wittig reactions within the confines of a chiral host, see: Toda, F.; Akai, H. *J. Org. Chem.* **1990**, *55*, 3446–3447.

(22) Pinsard, P.; Lellouche, J. P.; Gree, R. *Tetrahedron Lett.* **1990**, *31*, 1137–1140.

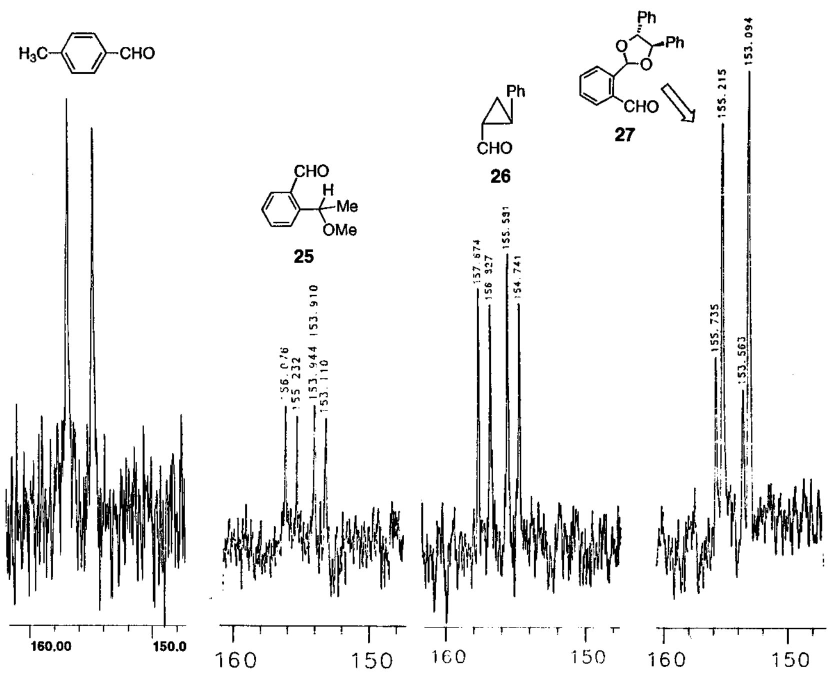
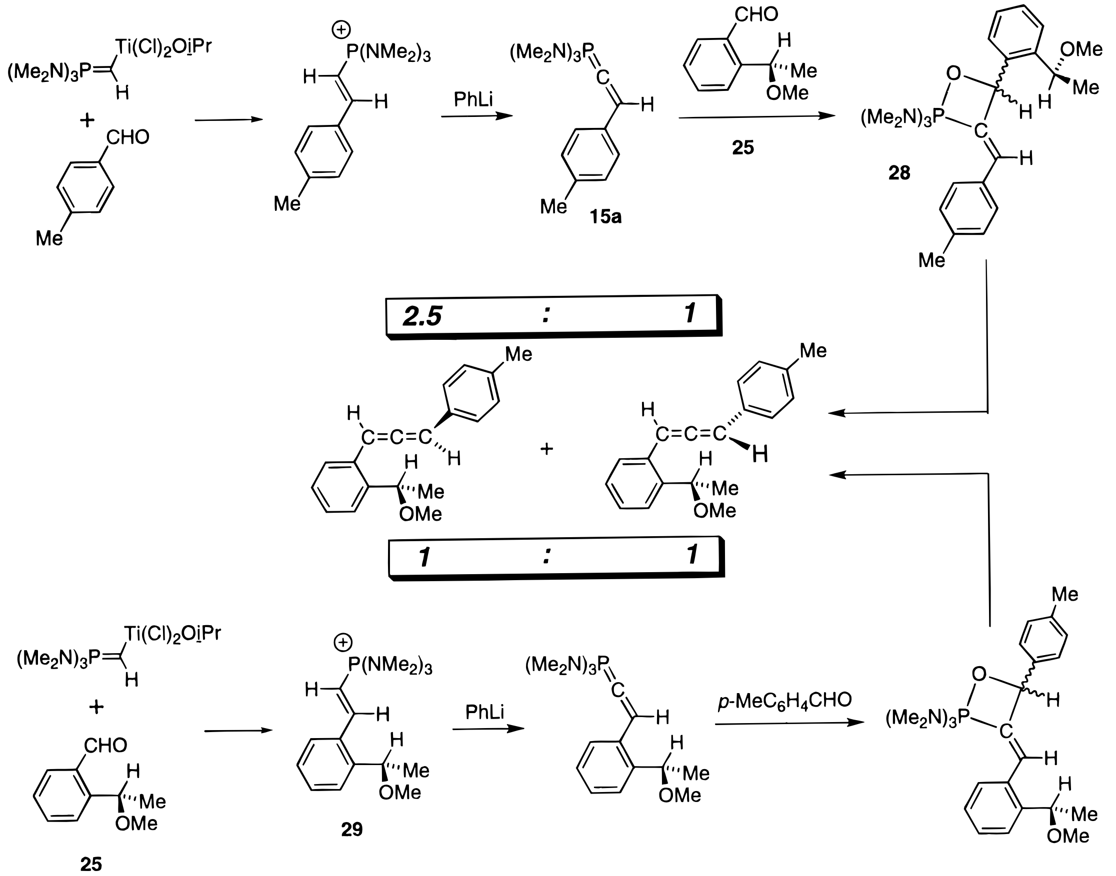


Figure 8. ^{13}C NMR spectra of oxaphosphetanes derived from **15a** and the indicated aldehyde.

Scheme 8



allene product under one-pot conditions shows that, of the 4 equiv of NaN(SiMe$_3$)$_2$ added to adduct **3**, 2 equiv are used in deprotonation and ligand substitution, consistent with the formation of species such as **33**. Extra base may participate in reversible coordination (i.e., to give **34**), but remains available in the reaction; this excess base acts to complex an equimolar amount of aldehyde. The dissociation of α-amino alkoxide must be slow on the timescale of the allene-forming reaction, since the complexed aldehyde does not participate in the double olefination reaction (Scheme 3).

On the basis of NMR data in comparison with known systems,[4c,d,f,23,24] we conclude that Ti-substituted ylide complexes **5** and **6**, like their metallocene counterparts,

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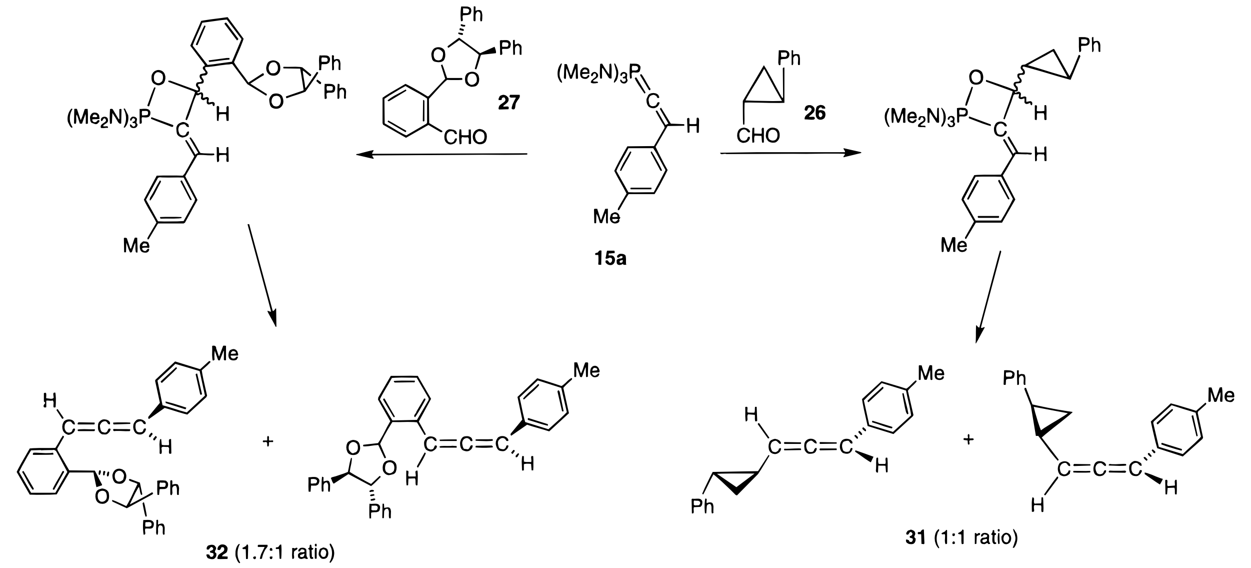
[23] (a) Johnson, A. W. *Ylides and Imines of Phosphorus;* John Wiley and Sons, Inc.: New York, 1993; p 55. (b) Breimaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy;* VCH: Weinheim (Federal Republic of Germany), 1990; pp 250–254.

Scheme 9



have substantial Ti−C double bond character.[25] Metal complexes such as **5**, **6**, and **33** may therefore be classified as "stabilized" ylides, in which the electron density at the ylide carbon is delocalized onto its substituent(s). The dependence of the yields of allenes and vinylphosphonium salts on the number of NMe$_2$ groups on phosphorus (Table 3 and Scheme 4) is consistent with the expectation that electron-donating groups on phosphorus are required to counteract the reduction in nucleophilicity of the ylide moiety brought about by the electron-withdrawing and bulky titanium substituent.[26] The electron-donating ability of the NMe$_2$ substituents is illustrated by the planarity of the Me$_2$N−P units in the crystal structures of adduct **3** reported here and vinylphosphonium salt **3x** described in the preceding paper.[27]

The Role of Base in One-Pot vs Stepwise Double Olefinations. A revealing difference between one-pot and stepwise processes is the nature of the bases employed. For the former methodology, an excess of NaN(SiMe$_3$)$_2$ provides the highest yields of allenes. Three factors are important: (1) the base cleanly deprotonates both the acidic ylide−Ti adducts and the vinylphosphonium salts while being too hindered to undergo conjugate addtion to the vinylphosphonium cation; (2) the aldehyde adduct of bis(trimethylsilyl)amide is itself quite basic, which is necessary to achieve the second deprotonation event, but is also readily dissociated upon workup, avoiding the production of large quantities of other organic products, as would occur with an alkyl- or aryllithium reagent; and (3) the base undergoes a limited set of substitution reactions with the titanium center, again making for a cleaner reaction mixture.

However, when the two olefination steps are conducted separately, the second is much more efficiently performed with phenyllithium than with bis(trimethylsilyl)amide. That the same base does not accomplish the same transformation in both one-pot and stepwise methodologies is due to differences in deprotonation rate, which are matched to the different reaction conditions. The one-pot reaction is conducted at room temperature, at which allenic phosphorane decomposes rapidly. It is therefore advantageous to generate it in small quantities at any one time and to trap it immediately as it is formed. The hindered nature of the bis(trimethylsilyl)amide base and the excess of aldehyde present under one-pot conditions accomplish these goals. Phenyllithium cannot be used because it is too reactive with other reaction components (aldehyde, titanium). In contrast, the deprotonation of isolated vinylphosphonium salts is best done at low temperature, where the allenic phosphorane can be generated in quantity and subsequently trapped with a stoichiometric amount of the second carbonyl component. At −78 °C, NaN(SiMe$_3$)$_2$ is not reactive with vinylphosphonium salts, and so the less hindered phenyllithium is employed.

Step 1: Vinylphosphonium Formation. Scheme 10 shows the proposed pathway for the production of vi-

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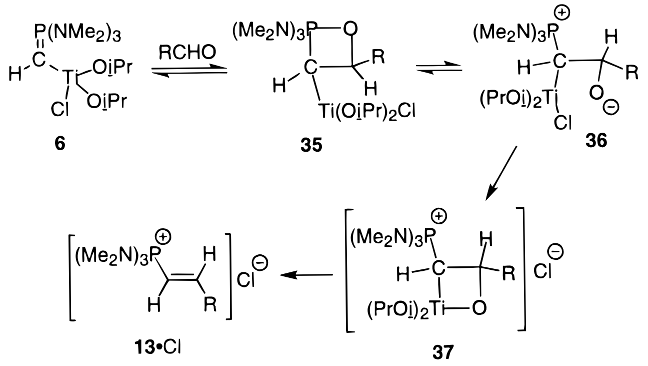
[24] (a) de Boer, H. J. R.; Akkerman, O. S.; Bickelhaupt, F.; Erker, G.; Czisch, P.; Mynott, R.; Wallis, J. M.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 639−640. (b) Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Organometallics* **1985**, *4*, 1310−1312. (b) Erker, G.; Czisch, P.; Mynott, R. *Z. Naturforsch., B*, **1985**, *40*, 1177−1183. (c) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729−1732.

[25] Characteristic of metal substitution are downfield shifts of the ylide carbon ^{13}C NMR signal and small ${}^{1}J_{CP}$ coupling constants in comparison to the parent methylides, indicative of diminished carbon−phosphorus overlap.[4g,23] For example, group 4 metallocene-substituted ylides bearing the Ph$_3$P moiety, Ph$_3$P=CH−M [M = Cp$_2$Ti-alkyl, Cp$_2$Zr−alkyl, Cp$_2$Hf−alkyl, and (η5-C$_5$Me$_4$(CH$_2$)$_3$OMe)TiCl$_2$], display ${}^{1}J_{CP}$ in the range of 11−37 Hz, suggesting a large contribution from the zwitterionic resonance form Ph$_3$P$^+$−CH=[TiCl$_2$Cp′]$^-$. While ${}^{1}J_{CP}$ values are larger in general for (Me$_2$N)$_3$P-bearing ylides than for triarylphosphine analogues, ^{31}P and ylide ^{13}C NMR resonances for complexes **5** and **6** are very similar to titanocene- and zirconocene-substituted complexes bearing the (Me$_2$N)$_3$P group (Figure 2),[8] and show similar drops in ${}^{1}J_{CP}$ when compared to (Me$_2$N$_3$)P=CH$_2$ (90−100 Hz compared to 175 Hz).

[26] The presence of electron-donating substituents on phosphorus is known to increase ylide nucleophilicity at carbon: (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley and Sons, Inc.: New York, 1985; pp 850−851 and references therein. (b) Johnson, A. W.; LaCount, R. B. *Chem. Ind.* **1959**, 52. (c) Johnson, A. W.; LaCount, R. B. *Tetrahedron* **1960**, *9*, 130−138.

[27] For vinylphosphonium salt **3x** in the preceding paper, the nitrogen atoms lie only 0.134 (N1), 0.084 (N2), and 0.041 (N3) Å out of the least-squares planes defined by the surrounding carbon and phosphorus centers; C−N−C bond angles are in the range 112−114°, while P−N−C bond angles are 120−126°. These parameters show that each dimethylamino group is considerably flattened. (The poor crystal quality of vinylphosphonium salt **3t** does not allow for this type of detailed comparison.) In contrast, for adduct **3** reported here, one of the Me$_2$NP units is substantially more compressed than the others, as shown by the out-of-plane distances of each nitrogen center: 0.197 Å (N1), 0.218 Å (N2), and 0.022 Å (N3) Å. Interestingly, the atoms C6, C7, N3, P1, C1, and Ti lie in the same plane, and the thermal ellipsoids of the C6/C7/N3 dimethylamino unit are strongly elongated normal to this plane, perhaps indicating that the N3 pπ-orbital provides resonance donor stabilization to phosphonium-Ti fragment.

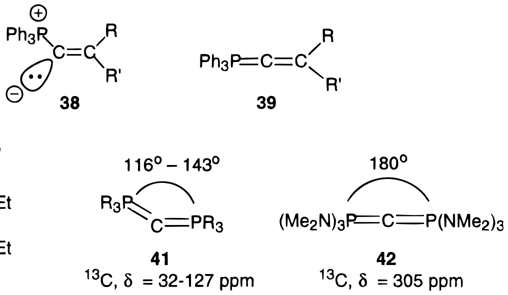
Scheme 10



nylphosphonium salts from Ti-substituted ylides and aromatic aldehydes. Wittig reactions are generally assumed to proceed via an oxaphosphetane without the prior intermediacy of a betaine.[17,28,29] If the reaction of titanium-substituted ylide and aldehyde follows the same course, the clean elimination of titanium oxides requires that a β-oxidophosphonium species **36** be formed by rapid ring opening of oxaphosphetane **35**.[30] The formation of vinylphosphonium salts and vinylphosphonates by elimination of stable metal or metalloid oxides has been previously observed,[3c,h;31−34] but eliminations the other way (losing phosphine oxide to give vinylmercurial[35] or vinylsilane[36] species) have also been noted. In the present case, we believe that titanium oxide formation is facilitated by the presence of a chloride ligand on the metal, providing a good leaving group for the formation of the four-membered titanoxacycle **37**.[37] Analogous complexes lacking a metal halide (i.e., those derived from monohalide precursors) perform poorly (Table 2, entries 4 and 15). In addition, the dimethylamino groups on phosphorus serve to stabilize the product vinylphosphonium cation. The selective production of (*E*)-vinylphosphonium salts provides no additional insight into the mechanism, since any (*Z*)-isomers that may be formed would spontaneously isomerize to the (*E*)-configuration, as shown in the preceding paper. It should also be noted that the enhanced Ti═C double bond character discussed above could provide for metal alkylidene-like reactivity in which the aldehyde oxygen interacts with titanium throughout the process. However, one might then expect metallocene-substituted ylides to undergo similar reactions, which is not observed.

Step 2: Allenic Phosphorane Generation and Reactivity. Amino-substituted ylides have not been extensively employed as Wittig reagents, so relatively little is known of their reactivity compared to the more common triphenylphosphorus or trimethylphosphorus compounds.[38]

Scheme 11



When used in Wittig reactions, the amino-substituted ylides give predominantly *trans* alkene products.[39] The pattern of fast attack of the ylide on a carbonyl electrophile followed by slow decomposition of the intermediate to alkene and phosphorus oxide, observed here for allenic phosphorane **15a**, was first reported for aminophosphorus ylides by Wittig.[39a]

The formation of allenic phosphorane **15a** from vinylphosphonium salt **13a** and PhLi was monitored by ^{13}C and ^{31}P NMR, showing an unexpected loss of observed ^{31}P−^{13}C coupling (Figure 3A). The presence of lithium cations may be responsible for the line broadening as these species are known to interact with phosphorus ylides, causing shifts in ^{31}P resonances and dramatic decreases in phosphorus−carbon coupling constants.[40] Accordingly, the structure of the allenic phosphorane unit is not clear; possibilities range from the bent structure **38** to the linear **39** (Scheme 11). The most closely related analogue to have been structurally characterized is allenic phosphorane **40**, which adopts a bent conformation in the solid state with concomitant localization of negative charge on the ylide carbon.[36,41,42] However, the substituents on the terminal carbon (C_β) are much different in the present case, and electron-donating substituents on phosphorus have been shown to promote a linear geometry in carbodiphosphoranes. Alkyl- and arylphosphine cases (**41**) are bent,[43] whereas the hexakis(dimethylamino) carbodiphosphorane **42** is perfectly linear,[44] a difference reflected in the ^{13}C NMR chemical shift of the central carbon atom, as shown. The downfield

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(28) Vedejs, E.; Peterson, M. J. *Topics Stereochem.* **1994**, *21*, 1−157.

(29) (a) Vedejs, E.; Marth, C. F. *J. Am. Chem. Soc.* **1990**, *112*, 3905−3909. (b) Mari, F.; Lahti, P. M.; McEwen, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 813−821. (c) Vedejs, E.; Marth, C. F. *J. Am. Chem. Soc.* **1988**, *110*, 3948−3958.

(30) Rapid ring opening of oxaphosphetanes to betaines is common for Wittig reactions of stabilized ylides.[17]

(31) Plénat, F. *Tetrahedron Lett.* **1981**, *22*, 4705−4709.

(32) Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 939.

(33) Tilhard, H.-J.; Ahlers, H.; Kauffman, T. *Tetrahedron Lett.* **1980**, *21*, 2803−2806.

(34) Savignac, P.; Teulade, M.-P.; Collignon, N. *J. Organomet. Chem.* **1987**, *323*, 135−144.

(35) Steiner, M.; Pritzkow, H.; Grützmacher, H. *Chem. Ber.* **1994**, *127*, 1177−1183.

(36) Bestmann, H. J. *Pure Appl. Chem.* **1980**, *52*, 771−788.

(37) When the analogous sequence is performed with TiCl(OiPr)$_3$, giving rise to a Ti-substituted ylide species that lacks a chloride ligand on titanium, very low yields of vinylphosphonium salts are obtained.

(38) Dialkylaminophosphorus ylides are generally thermally stable; however, the methylides and other ylides lacking stabilizing groups on the ylide carbon are extremely sensitive to moisture and in some cases may be oxidized rapidly by atmospheric oxygen. $(Me_2N)_3P{=}CH_2$ was found to be stable under inert atmosphere at room temperature for several months but "smokes" when exposed to air, which necessitated handling in the glove box. In comparison to most aryl-substituted phosphorus ylides, the amino substitution offers two practical advantages: the corresponding phosphine oxide, HMPA, is water soluble, and the greater reactivity of the starting phosphine, HMPT, makes the synthesis of precursor phosphonium salts extremely facile. Considering stereochemical outcome, ylide thermal stability, and isolability, these species appear to be best classified as stabilized to semistabilized ylides, but are much more basic than typical stabilized ylides that bear substituents to delocalize the negative charge on the ylide carbon.

(39) (a) Wittig, G.; Weigmann, H.-D.; Schlosser, M. *Chem. Ber.* **1961**, *94*, 676. (b) Oediger, H.; Eiter, K. *Liebigs. Ann. Chem.* **1965**, *682*, 58.

(40) Schweizer, E. E.; Albright, T. A. *J. Org. Chem.* **1976**, *41*, 1168−1173.

(41) Bestmann, H. J.; Voll, U.; Burzlaff, H. *Chem. Ber.* **1974**, *107*, 1949.

(42) (a) Bestmann, H. J.; Sandmeier, D. *Chem. Ber.* **1980**, *113*, 274−277. (b) Bestmann, H. J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 349−364. (c) Saalfrank, R. W. *Tetrahedron Lett.* **1975**, 4405−4408. (d) Bestmann, H. J.; Saalfrank, R. W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 367−368. (e) Daly, J. J.; Weathley, P. *J. Chem. Soc. A* **1966**, 1703.

(43) Johnson, A. W. *Ylides and Imines of Phosphorus;* John Wiley and Sons, Inc.: New York, 1993; Chapter 10.

(44) Appel, R.; Baumeister, U.; Knoch, F. *Chem. Ber.* **1983**, *116*, 2275−2284.

chemical shift of allenic phosphorane **15a** (185 ppm) and the lack of donor groups at the C_β position suggest that **15a** may adopt a more linear structure than **40** and helps explain the lack of reactivity of these allenic phosphoranes with less electrophilic substrates such as ketones.

Oxaphosphetane Stability. Oxaphosphetanes from standard stabilized ylides have never been directly observed,[45] and oxaphosphetanes from unstabilized ylides are usually characterized only by low temperature NMR.[46,47] The greater stability of allenic phosphorane-derived oxaphosphetanes noted above in our NMR studies apparently derives from the electron-rich nature of the $(Me_2N)_3P$ moiety, which diminishes the strength of the phosphorus−oxygen interaction that is integral to the decomposition process.[26a] Note that the use of a trifluoromethyl group in **18** provides for an even more robust oxaphosphetane, in analogy to previous examples.[48,49]

The coexistence of oxaphosphetane **16** and betaine **17** forms in some samples is proposed from NMR data summarized in Figures 3−7; the composition of each mixture is sensitive to concentration and the amount of excess aldehyde present. This suggests that intermolecular effects such as aggregation are important in determining the relative distribution of these species, which is reasonable in the presence of $LiBPh_4$ and lithium alkoxide salts generated from the quenching of excess PhLi with excess aldehyde. The temperature-dependent disappearance of NMR resonances for both species before the appearance of product allene and HMPA signals strongly suggests that oxaphosphetane and betaine interconvert at rates that produce severe line broadening, with phosphine oxide elimination occurring before a temperature can be reached at which a coalesced resonance can emerge. The observation of interconverting oxaphosphetane and betaine isomers appears to be unusual.[17,51b] The formation of allenes by a Wittig-like elimination step involving the treatment of a discrete (β-hydroxyvinyl)phosphine oxide with base has been reported.[50]

While most Wittig reactions are under kinetic control, such that the ratio of *cis* and *trans* alkenes obtained is the same as the initial ratio of oxaphosphetane isomers formed,[17,26a,28,51] certain reactions display a mismatch between these quantities in favor of the thermodynamically more stable alkene isomer, in a phenomenon termed “stereochemical drift”.[17,51b,52,53] Two such cases are noted above for oxaphosphetanes and product allenes from aldehydes **25** and **27** (Figure 8 and Scheme 8), suggesting that the oxaphosphetane-forming condensation of allenic phosphorane with aldehyde is reversible. Conditions which are known to promote stereochemical drift, and which therefore have been suggested to promote reversible C−C bond formation, include the presence of lithium salts, the use of aromatic aldehydes, and the presence of electron-donating groups at phosphorus,[49a] all of which are found in the present examples. However, complete dissociation of oxaphosphetanes/betaines **16a/17a** and **16b/17b**, derived from achiral aldehydes, is ruled out by the lack of crossover products when these intermediates are treated with different aldehydes at low temperature prior to allene formation (Scheme 6, Figures 4 and 5). A mechanism that allows for epimerization at one stereogenic center but not for reversible phosphorane−oxaphosphetane interconversion is necessary to accommodate these observations. Betaine intermediates of general structure to **17** are proposed to undergo equilibrium isomerization of the olefinic moiety either directly via the benzylic cation resonance form (which has precedent in the isomerization of *Z*- to *E*-vinylphosphonium salt reported in the preceding paper) or by the reversible formation of an oxetane ylide **43**, which would also result in the scrambling of betaine C−O bonds. This scenario will be probed in greater detail as new chiral substituents for phosphorus are developed for enantioselective allene formation.

Asymmetric Induction. The presence of phosphorus, and not titanium, in the allene-forming deoxygenation step of the one-pot condensation process was verified by the observation of asymmetric induction (albeit at a low level) using *ortho*-substituted arylbis(dimethylamino)phosphorus ylides (Scheme 7) and the production of racemic allene when a chiral titanium alkoxide species was employed. Unfortunately, yields of allenes are low if more than one dimethylamino group is replaced by an aryl unit (Table 3), so the wide variety of known chiral alkyl- and aryl-substituted phosphorus reagents cannot be used in this process. Ylides derived from other chiral 1,2-diamines are currently being developed.

The presence of a chiral moiety, incorporated into either the trapping aldehyde or the allenic phosphorane, creates the potential for the formation of diastereomeric oxaphosphetanes, which can be detected by ^{13}C NMR. Unsurprisingly, when the chiral auxiliary is placed far from the oxaphosphetane nucleus, as occurs with phenylcyclopropanecarboxaldehyde **26**, no diastereomeric induction is observed (Scheme 9). More revealing is the case of *o*-(2-methoxyethyl)benzaldehyde (**25**), which also gives a 1:1 diastereomer ratio when converted to vinylphosphonium salt and subsequently condensed with an achiral aldehyde. The same allene is formed in 43% de when **25** is used to trap the appropriate achiral allenic phosphorane (Scheme 8). The structures of the intermediate oxaphosphetanes provide a convenient rationalization for this observation. In the former case, the two oxaphosphetane chiral centers are far apart, whereas the latter case (Scheme 8, structure **28**) places them adjacent to one another, thus leading to diastereomeric discrimination only in the second example.

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(45) (a) Reference 23a; Chapter 9. (b) An exception is the work of the Vedejs group using allylylides and benzylides having a sterically stabilized benzodiphosphole group: see reference 49a.

(46) For a recent related example, see Wilker, S.; Laurent, C.; Sarter, C.; Puke, C.; Erker, G. *J. Am. Chem. Soc.* **1995**, *117*, 7293−7294, and reference 1 therein.

(47) Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 2823−2831.

(48) (a) Kawashima, T.; Kato, K.; Okazaki, R. *J. Am. Chem. Soc.* **1992**, *114*, 4008−4010. (b) Kawashima, T.; Kato, K.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 869−870. (c) Birum, G. H.; Matthews, C. N. *J. Org. Chem.* **1967**, *32*, 3554−3559. (d) Ramirez, F.; Smith, C. P.; Pilot, J. F. *J. Am. Chem. Soc.* **1968**, *90*, 6726−6732. (e) Ul-Haque, M.; Caughlin, C. N.; Ramirez, F.; Pilot, J. F.; Smith, C. P. *J. Am. Chem. Soc.* **1971**, *93*, 5229−5235. (f) Kolodiazhnyi, O. I.; Ustenko, S. N. *Phosphorus Sulfur*, **1991**, *62*, 111. (g) Bestmann, H. J.; Roth, K.; Wilhelm, E.; Böhme, R.; Burzlaff, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 876−877.

(49) (a) Vedejs, E.; Marth, C.; Ruggeri, R. *J. Am. Chem. Soc.* **1988**, *110*, 3940−3948. (b) Vedejs, E.; Marth, C. F. *J. Am. Chem. Soc.* **1988**, *110*, 3948−3958.

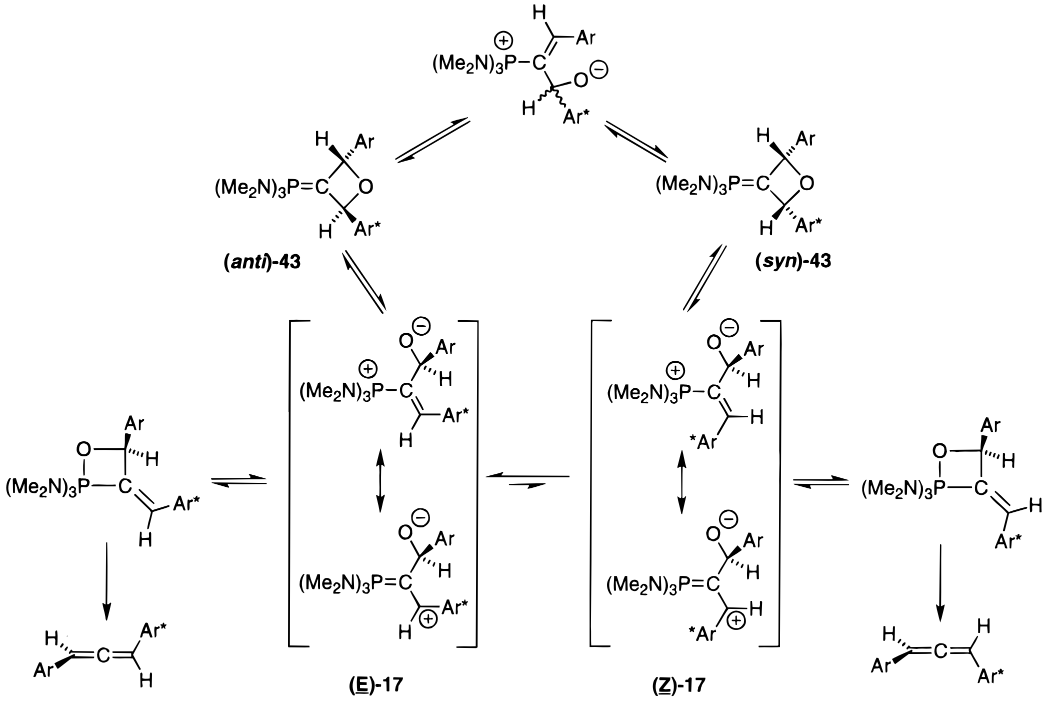
(50) Marszak, B.; Simalty, M.; Seuleiman, A. *Tetrahedron Lett.* **1974**, 1905−1908.

(51) (a) Schlosser, M.; Schaub, B. *J. Am. Chem. Soc.* **1982**, *104*, 5821−5823. (b) Reitz, A. B.; Mutter, M. S.; Maryanoff, B. E. *J. Am. Chem. Soc.* **1984**, *106*, 1873−1875.

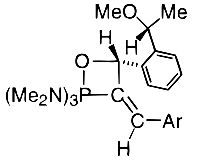
(52) (a) Maryanoff, B. E.; Reitz, A. B.; Mutter, M. S.; Inners, R. R.; Almond, H. R.; Whittle, R. R.; Olofson, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 7664−7678. (b) Maryanoff, B. E.; Reitz, A. B.; Mutter, M. S.; Ineers, R. R.; Almond, H. R., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 1068−1070.

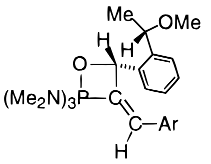
(53) Reference 23a, Chapter 9, pp 286−291, and references therein.

Scheme 12



The importance of relative rates of oxaphosphetane decomposition is illustrated by the case of aldehyde **25**, which gives a 1:1 ratio of oxaphosphetane diastereomers at low temperature and decomposes to a 7:3 ratio of allenes. This amounts to approximately a 2-fold difference in the rate of decomposition of oxaphosphetane structures **44** and **45**, shown for clarity as being epimeric at the benzylic substituent. The origin of this rate difference is intriguing and not obvious. We speculate that one diastereomeric structure may allow easier interaction between phosphorus and the methyl ether as the P−C bond breaks during decomposition, perhaps speeding the process. Definitive conclusions about such mechanistic details must await additional results.


44


45

A summary of the important observations and conclusions includes the following points.

(1) The use of titanium alkoxide instead of titanium amide precursors allows for the clean and convenient isolation of monometalated phosphorus methylide species. A mixture of active complexes is formed in the presence of excess bis(trimethylsilyl)amide base, which are proposed to arise from reversible $N(SiMe_3)_2$ coordination to the metal. The number and steric bulk of such complexes is diminished when $TiCl_2(O\textit{i}Pr)_2$ is employed instead of $TiCl_3(O\textit{i}Pr)$, so the former reagent is now recommended in all cases.

(2) These phosphorus−titanium compounds react with aromatic and certain nonenolizable aliphatic aldehydes to give vinylphosphonium salts. The selective elimination of titanium oxide byproducts, rather than phosphine oxide, is proposed to arise from the presence of a chloride leaving group on titanium.

(3) Excess bis(trimethylsilyl)amide base reacts with aromatic aldehydes to give α-amino alkoxides, which are also competent bases for the deprotonation of vinylphosphonium salts. The formation of an α-amino alkoxide makes its aldehyde component unavailable for condensation with allenic phosphorane. Thus, when excess $NaN(SiMe_3)_2$ must be used to boost the rate of deprotonation of intermediate vinylphosphonium species (as in the one-pot double olefination process), an even larger excess of aldehyde is required. However, the aldehyde used to trap allenic phosphorane need not be the same as the one used to generate vinylphosphonium and complex excess bis(trimethylsilyl)amide, allowing for selective incorporation of different aldehydes even under "one-pot" conditions.

(4) Dimethylamino-substituted phosphorus components are required for high yields in both steps of the allene-forming process, presumably to boost the reactivity of the hindered Ti-substituted ylide reagents and to stabilize the allenic phosphorane unit so that it may be trapped by aldehyde.

(5) The reaction of allenic phosphoranes with aldehydes affords oxaphosphetane and betaine intermediates in varying ratios with different reaction conditions. These species appear to interconvert upon warming with subsequent production of allene and phosphine oxide.

(6) The placement of chiral groups on the phosphorus methylide or aldehyde components results in low levels of diastereomeric induction in allene formation. In two cases, the diastereomeric ratios of initially-formed oxaphosphetanes differ from the diastereomeric composition of their product allenes (an example of "stereochemical drift"). However, oxaphosphetane/betaine formation from allenic phosphorane and aldehyde has been found to be irreversible, suggesting that an intramolecular betaine olefin isomerization is responsible for the loss of stereochemical integrity during the Wittig step.

(7) In addition to its application in the selective synthesis of mixed allenes, the two-step procedure involving isolated vinylphosphonium salts proceeds under conditions that are less basic than the original one-pot

procedure. The reaction scope is thereby enhanced to some degree, and two routes to any target allene are made available for optimization. Future development of the synthetic methodology must focus on modifications that allow for the general conversion of aliphatic aldehydes and ketones into allenes.

Experimental Section

General Methods. ^{1}H,^{13}C, and ^{31}P NMR spectra were recorded at 300, 75.2, and 121.7 MHz, respectively; ^{31}P spectra were referenced to external H_3PO_4. ^{13}C and ^{31}P NMR spectra recorded on THF solutions were either run in unlocked mode, or approximately 10% C_6D_6 was added by volume for spectrometer locking; very small differences in line widths and peak positions were noted for these two methods. The downfield THF resonance in these ^{13}C NMR experiments was used as the chemical shift reference (67.4 ppm).

THF, hexane, and toluene were purified by distillation from Na benzophenone-ketyl; CH_2Cl_2 and $CDCl_3$ were purified by distillation from P_4O_{10}; C_6D_6 was bulb-to-bulb distilled from a sodium mirror; all solvents were stored under inert atmosphere over activated 4 Å molecular sieves. $Ti(OiPr)_4$ was distilled under vacuum and stored in an inert-atmosphere drybox. See the note about $TiCl_3OiPr$ in the Experimental Section of the preceding paper, under "Vinylphosphonium Method B". $(Me_2N)_3P{=}CH_2$ and PhLi were prepared as discussed in the accompanying paper. All other reagents were purchased from commerical suppliers and used as received. No differences were noted for reactions using $NaN(SiMe_3)_2$ purchased as a solid or in THF solution. All manipulations involving titanium and ylide species were conducted under dry nitrogen atmosphere, either using standard Schlenk techniques or in a drybox. Unless otherwise indicated, one-pot allene syntheses were performed using procedures directly analogous to that of the original report,[1] which is repeated below along with an improved one-pot technique. Characterization data for most of the allenes reported here are given in the preceding paper.

Complex 3. A solution of $TiCl_2(OiPr)_2$ (70 mg, 0.30 mmol; prepared as a white or light yellow solid from $TiCl_4$ + $Ti(OiPr)_4$ in CH_2Cl_2, stable on extended storage) in 5 mL of toluene was added dropwise to $TiCl_4$ (56 mg, 0.30 mmol) in 5 mL of toluene. The resulting solution of $TiCl_3OiPr$ was added dropwise to a solution of $(Me_2N)_3P{=}CH_2$ (105 mg, 0.059 mmol) in 50 mL of toluene, causing an immediate orange and then deep red color. Upon cooling to −30 °C, complex **3** precipitates as large, orange, air-sensitive crystals suitable for X-ray analysis, which were washed with toluene and dried *in vacuo* (172 mg, 0.44 mmol, 74% yield). ^{1}H NMR (C_6D_6, δ) 5.00 (m, 1H), 2.99 (d, $^2J_{PH}$ = 9.3 Hz, 2H), 2.10 (d, $^3J_{PH}$ = 9.6 Hz, 16H), 1.34 (d, J_{HH} = 6.3 Hz, 6H); ^{13}C NMR (THF, δ) 32.99 (d, $^1J_{PC}$ = 82.5 Hz; undecoupled spectrum shows dt, $^1J_{CH}$ = 122.5 Hz. Upon standing in THF solution for several hours, a single new ^{13}C-enriched species appears at 8.2 ppm, corresponding to $[(Me_2N)_3PCH_3]^+$.

Complex 4. Treatment of $TiCl_2(OiPr)_2$ with an equimolar amount of $(Me_2N)_3P{=}CH_2$ in C_6D_6 gives rise to a red solution containing **4** and methylphosphonium species $[(Me_2N)_3PCH_3]^+$. The latter compound is produced rapidly at the expense of **4** upon standing. For **4**, extracted from NMR spectra recorded immediately after mixing at room temperature: ^{1}H NMR (C_6D_6, δ) 5.26 (br m, 2H), 2.4 (m, 20H), 1.5 (br s, 12H); ^{13}C NMR (C_6D_6, δ) 83.1, 37.5, (d, $^1J_{PC}$ = 84.9 Hz), 25.8.

Complex 6. $TiCl_2(OiPr)_2$ (0.067 g, 0.283 mmol) in hexane was treated with a hexane solution of $(Me_2N)_3P{=}^{13}CH_2$ (0.050 g, 0.281 mmol). The resulting red mixture was treated immediately with $NaN(SiMe_3)_2$ (0.255 g of 1.106 mmol/g solution in THF, 0.282 mmol) at room temperature, causing a color change to deep red. In THF solution, ^{13}C NMR shows a major species at 124.4 ppm (d, $^1J_{PC}$ = 102.7 Hz); ^{31}P under the same conditions shows a dominant resonance at 58.2 ppm (d, $^1J_{PC}$ = 103.5 Hz).

Ylide Complexes in the Presence of Varying Equivalents of $NaN(SiMe_3)_2$ (Table 1). Adduct **3** was generated *in situ* by the addition of a THF solution of $(Me_2N)_3P{=}^{13}CH_2$ to an equimolar amount of $TiCl_3OiPr$ in hexane−THF (approximately 0.6 mmol scale). To this solution was added varying amounts of $NaN(SiMe_3)_2$ in THF, as indicated in Table 1. ^{13}C NMR spectra were recorded within 30 min at ambient temperature.

Complex 7. To 0.60 mmol of $TiCl_3OiPr$ in 5 mL of hexane−THF solution was added $(Me_2N)_3P{=}CH_2$ (99 mg, 0.56 mmol), followed by 2.4 mmol of $NaN(SiMe_3)_2$ in THF, giving a dark red-brown solution. The solvent was removed by rotary evaporation and the resulting glassy orange solid resuspended in a mixture of 20 mL of hexane plus 3 mL of benzene. The reaction mixture was stirred for 20 min and filtered through a medium frit to remove a small amount of light brown precipitate. The transparent red-brown filtrate was concentrated in vacuo to be a viscous dark-reddish oil. ^{13}C NMR shows one doublet resonance at 115.3 ppm ($^1J_{PC}$ = 97.2; CH by DEPT), in addition to one major set of remaining signals that includes two resonances for isopropoxide groups in different environments. Two broad isopropoxide methine multiplets are also observed in the ^{1}H NMR spectrum. At least six signals for $SiMe_3$ groups appear in both ^{13}C and ^{1}H NMR spectra, which are included in the Supporting Information. A ^{13}C,^{1}H-correlated 2D-NMR spectrum is also presented, confirming the assignment of the ^{13}C 115.3/^{1}H 5.52 resonances as the ylide P−*CH*−Ti unit.

$TiCl_2(OiPr)[N(SiMe_3)_2]$. A freshly prepared solution of $TiCl_3(OiPr)$ (2.24 mmol) in THF was treated with $NaN(SiMe_3)_2$ (2.02 g of a 1.107 mmol/g stock solution in THF; 2.24 mmol) by pipette, causing a color change to cloudy dull yellow-orange. The reaction mixture was stirred for 10 min, and solvent was removed by rotary evaporation to produce an amorphous solid. NMR reveals the presence of two species in a ratio of approximately 1:1.5, presumably complexes of differing aggregation state or structure. ^{1}H NMR (C_6D_6, δ, major species resonance marked with an asterisk) 4.63 (m), 4.43* (br quintet, 1H for sum of both resonances), 3.96 (br s, THF), 1.18 (d, J = 5.4 Hz), 1.12* (d, J = 5.4 Hz, 6 H for sum of both resonances), 0.31 (br d, J = 6.6 Hz, 18 H); ^{13}C NMR (C_6D_6, δ) 88.6, 83.4, 72.8 (THF), 25.4, 25.1, 24.8 (THF) 5.4, 3.9. Use of this complex without isolation as the titanium species in the standard one-pot reaction[1] with 4-methylbenzaldehyde gave allene **12** in 50% isolated yield. An analogous sequence using 2 equiv of $NaN(SiMe_3)_2$ with respect to $TiCl_3OiPr$ gave a cloudy yellow solution which was stirred for approximately 10 min before the addition of $(Me_2N)_3P{=}CH_2$ (1 equiv with respect to titanium). No color change was observed, in contrast to all other ylide−Ti halide mixtures. Four equivalents of $NaN(SiMe_3)_2$ were added, also resulting in little change in the appearance of the solution. ^{13}C NMR of an aliquot (in THF) showed unreacted ylide (δ −9.9, $^1J_{CP}$ = 176 Hz). Addition of *p*-tolualdehyde to this mixture did not produce allene.

Aldehyde Adducts of $NaN(SiMe_3)_2$. Under dry nitrogen atmosphere, a sample of neat benzaldehyde (20 mg, 0.19 mmol) was treated with $NaN(SiMe_3)_2$ (0.342 g of a 1.107 mmol/g solution in THF; 0.38 mmol) and examined by ^{13}C NMR. The carbonyl resonance, previously at 191.8 ppm, was replaced by a new peak at 167.4 ppm. This peak was observed as a doublet when $Ph^{13}CHO$ was used. When electron-deficient aldehydes (for example, 4-Cl-, 4-Br-, or 4-CF_3-benzaldehyde, ca. 0.5 *M*) are treated in a similar fashion with 0.2 equiv of $NaN(SiMe_3)_2$, about half of the signature aldehyde resonance in the ^{13}C NMR disappears in favor of a new signal at approximately 165 ppm. The ratio of aldehyde and α-amino alkoxide is roughly proportional to overall concentration; when the solvent is removed by rotary evaporation and the residue taken up in C_6D_6, all of the aldehyde is observed to have disappeared.

General Procedure for One-Pot Allene Condensation Reactions. A THF solution of $TiCl_3OiPr$ was treated with a THF solution of $(Me_2N)_3P{=}CH_2$ and 4 equiv of $NaN(SiMe_3)_2$.. Alternately, the ylide can be added first followed by rapid addition of the base, producing a cloudy, deep red-brown solution. (However, a reversal of this order (base, then ylide) is inadvisable due to the formation of unreactive Ti−$N(SiMe_3)_2$ species.) An excess (generally 8 equiv) of the appropriate aldehyde was added to the titanium−ylide solution. Upon addition of the substrate, a rapid color change to yellow usually occurred, often accompanied by noticeable warming. The reactions were allowed to stand at room temperature for approximately 1 h and then worked up by partitioning between diethyl ether and a 10% solution of tartaric acid. The ether layer was reduced in volume and flash chromatographed (silica, mixtures of CH_2Cl_2 and light petroleum ether) to give the allenes.

While most of the screening experiments reported here (Scheme 4, Table 2, Table 3) were performed using the above procedure with the indicated variation in reaction components, we now recommend the use of $TiCl_2(O\textit{i}Pr)_2$ and 3 equiv of $NaN(SiMe_3)_2$, as in the following example. $TiCl_2(O\textit{i}Pr)_2$ (67 mg, 0.28 mmol) in 10 mL of THF was treated with $(Me_2N)_3P{=}CH_2$ (50 mg, 0.28 mmol) in 10 mL of THF dropwise with stirring, forming a bright orange solution. $NaN(SiMe_3)_2$ (384 mg in 2 mL of THF, 0.425 mmol) was added causing a color change to a cloudy red-brown. Immediately, 4-methylbenzaldehyde (60 mg, 0.50 mmol) was added with vigorous stirring, and the reaction mixture was allowed to stand for 1 h at room temperature before workup and chromatography as described above to afford allene **12** (62 mg, 70% yield).

Screening Metal Halide Components (Table 2). The appropriate metal halide reagent was dissolved or suspended in THF and treated dropwise with stirring with 1 equiv of $(Me_2N)_3P{=}CH_2$. The reaction mixture was stirred for 1−2 min, and then 4 equiv of $NaN(SiMe_3)_2$ in THF were added, and the reaction was stirred for an additional 1−5 min. Excess aldehyde (at least 8 equiv) was added, and the reactions were typically stirred for at least 4 hours before workup. Allene is easily identified as a nonpolar spot on TLC (silica, 10% CH_2Cl_2 in light petroleum ether) or by ^{13}C NMR of the crude reaction product. Yields reported in Table 2 are of allenes showing clean NMR spectra, isolated by column chromatography.

Screening Phosphorus Components for One-Pot Allene Formation (Table 3). Where the purified ylides were available (Table 3, entries 1, 9−11), allene condensations were carried out by the standard one-pot procedure described above, substituting the appropriate ylide for $(Me_2N)_3P{=}CH_2$. Where phosphonium salts were employed (Table 3, entries 2−8), the salt was suspended in THF and 1−1.5 equiv of $NaN(SiMe_3)_2$ was added and stirred for approximately 1 h to generate the ylide *in situ*. The resulting mixture was then used in place of the standard methylide in the general procedure described above.

$[Ph(Me_2N)_2PCH_3]I$ and $[Ph_2(Me_2N)PCH_3]I$. The requisite phosphines were prepared from addition of PhLi to $(Me_2N)_2PCl$ and Me_2NPCl_2 (prepared by reaction of dimethylamine with PCl_3 and kindly provided by Mr. Kevin Dockery of the University of Utah) at −78 °C in THF and purified by vacuum distillation. $Ph(Me_2N)_2P$ (2.545 g, 12.98 mmol) in 60 mL of toluene was treated with CH_3I (5.85 g, 41.2 mmol), causing the immediate formation of a white precipitate. The reaction was stirred for 1 h, filtered, washed with diethyl ether, and dried under vacuum to obtain phosphonium salt $[Ph(Me_2N)_2PCH_3]I$ (4.12 g, 94%). ^1H NMR ($CDCl_3$, δ) 7.89−7.67 (m, 5H), 2.91 (d, $^3J_{PH} = 10.5$ Hz, 12 H), 2.57 (d, $^1J_{PC} = 12.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$, δ) 134.5, 131.8 (d, $^3J_{PC} = 11.3$ Hz), 129.9 (d, $^2J_{PC} = 13.5$ Hz), 121.2 (d, $^1J_{PC} = 122.0$ Hz), 37.5 (d, $^3J_{PNC} = 3.2$ Hz), 11.8 (d, $^1J_{PC} = 86.8$ Hz); ^{31}P NMR (CH_2Cl_2) 60.5. An analogous reaction was carried out with Ph_2PNMe_2 (1.19 g, 4.89 mmol) and CH_3I (2.71g; 19.1 mmol) to afford $[Ph_2(Me_2N)PCH_3]I$ (0.91 g, 50% yield). An additional 10% yield was obtained by cooling the filtrate to 0 °C for 12 h. ^1H NMR ($CDCl_3$, δ) 7.89−7.69 (m, 10 H), 2.92 (d, $^3J_{PH} = 10.8$ Hz, 6H), 2.93 (d, $^2J_{PH} = 12.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$, d) 135.7, 133.2 (d, $^2J_{PC} = 11.0$ Hz), 130.9 (d, $^3J_{PC} = 13.1$ Hz), 121.1 (d, $^1J_{PC} = 100.9$ Hz), 39.3, 13.0 (d, $^1J_{PC} = 67.6$ Hz); ^{31}P NMR (CD_3CN) 54.0.

$Ph(Me_2N)_2P{=}CH_2$ and $Ph_2(NMe_2)P{=}CH_2$ (Table 3, Scheme 4). A mixture of $[Ph(Me_2N)_2PCH_3]I$ (4.036 g, 11.9 mmol) and $NaNH_2$ (1.03 g, 26.4 mmol) was stirred in 200 mL of liquid NH_3 at −78 °C for 3 h. The reaction mixture was allowed to warm slowly to room temperature, evaporating the ammonia was evaporated, and then the mixture was transferred to an inert-atmosphere glovebox under vacuum. The solids were stirred with 150 mL of dry diethyl ether, and the resultant slurry was filtered through a medium frit. Removal of the solvent by rotary evaporation followed by vacuum distillation (93 °C, approximately 0.2 torr) of the resulting oil furnished $Ph(Me_2N)_2P{=}CH_2$ as a viscous yellow oil (1.129 g, 45% yield). ^1H NMR (C_6D_6, δ) 7.76−7.70 (m, 2H), 7.10−7.04 (m, 3H), 2.39 (d, $^3J_{PH} = 11.1$, 12H), 0.57 (d, $^2J_{PH} = 12.0$ Hz, 2H); ^{13}C NMR (C_6D_6, δ) 37.3, −4.97 (d, $^1J_{PC} = 150.3$ Hz). Use of $[Ph_2(Me_2N)PCH_3]I$ (0.844 g, 2.27 mmol) and $NaNH_2$ (0.211g, 5.4 mmol) in the above procedure, followed by evaporation of the ethereal filtrate, afforded $Ph_2(NMe_2)P{=}CH_2$ as a yellow-orange crystalline solid (0.384 g, 1.59 mmol, 70% yield.). ^1H NMR (C_6D_6, δ) 7.99−7.92 (m, 4H), 7.14 - 7.11 (m, 6 H), 2.41 (d, $^3J_{PH} = 11.7$ Hz, 6H), 0.93 (d, $^2J_{PH} = 8.7$ Hz, 2H); ^{13}C NMR (C_6D_6, δ) 132.5 (d, $^2J_{PC} = 8.5$ Hz), 130.7, 128.6 (d, $^3J_{PC} = 11.8$ Hz), 128.0 (d, $^1J_{PC} = 24.3$ Hz), 36.9, −1.1 (d, $^1J_{PC} = 120.5$ Hz).

13b (Scheme 4). $Ph(Me_2N)_2P{=}CH_2$ (0.414 g, 1.99 mmol) was treated with 1 equiv of $TiCl_3O\textit{i}Pr$, followed by 2 equiv of $NaN(SiMe_3)_2$ (3.60 g of a 1.106 mmol/g solution in THF, 3.98 mmol) to form a dark red-orange solution. Three equivalents of 4-methylbenzaldehyde (0.72 g, 6.0 mmol) were added, causing a color change to lighter orange and a precipitate. The reaction was stirred for 30 min and filtered, and the vinylphosphonium salt was **13b**·BPh_4 isolated by the standard technique described in the preceding paper ("method A") to yield 0.367 g (1.20 mmol, 60% yield). ^1H NMR (CD_3CN, δ) 7.80−7.59 (m, 8H), 7.39−7.36 (m, 1H), 7.31 (br s, 9H), 6.99 (t, $J = 7.2$ Hz, 8H), 6.83−6.72 (m, 6 H) 2.79 (d, $J = 10.2$ Hz, 12H) 2.38 (s, 3H) (Note: the characteristic dd vinyl peaks are hidden under aromatic resonances.); ^{13}C NMR (CD_3CN, δ)153.9 (d, $^2J_{CP} = 6.4$ Hz), 136, 135.3, 133.3, 133.2, 130.5, 130.2, 129.2, 126.0, 122.2, 106.5 (d, $^1J_{CP} = 129.8$ Hz), 37.3 (d, $^3J_{PNC} = 2.6$ Hz), 21.1; ^{31}P NMR (CH_3CN, δ) 52.6; UV-vis (CH_2Cl_2) 232, 278 (sh), 298; m.p. 138−140 °C.

13c (Scheme 4). A freshly prepared solution of $TiCl_3O\textit{i}Pr$ (0.300 mmol) in 1:2 hexane:THF was treated with 1 equiv of $NaN(SiMe_3)_2$ (0.269 g of a 1.106 mmol/g solution in THF, 0.298 mmol), followed immediately by 1 equiv of $Ph_2(Me_2N)P{=}CH_2$ (0.073 g, 0.300 mmol) to form a dark red-orange solution. (This order of addition was found to be slightly superior to the standard technique whereby methylide is introduced before $NaN(SiMe_3)_2$). Addition of an additional 1 equiv of $NaN(SiMe_3)_2$ caused a color change to a darker brown color. The solution was allowed to stir for approximately 1 min, and then excess 4-methylbenzaldehyde (0.178 g, 1.48 mmol, 5 equiv) was added causing a color change to pale orange-yellow. The mixture was allowed to stir for approximately 90 min and was then filtered through a medium frit. Anion exchange for BPh_4 was accomplished as described in the accompanying paper to yield **13c**·BPh_4 (0.040 g, 0.069 mmol, 23%) as a white solid. NMR data for the chloride salt, which suffers from fewer overlapping resonances, is given here: ^1H NMR ($CDCl_3$, δ) 8.00 (dd, $J_{HH} = 17.1$ Hz, $^2J_{PH} = 19.5$ Hz, 1H), 7.93−7.67 (m, 13 H), 7.30−7.17 (m, 3H), 2.95 (d, $^3J_{PNC} = 10.5$ Hz, 6H), 2.33 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 156.0 (d, $^2J_{CP} = 6.12$ Hz), 143.4, 135.5, 134.0, 133.9, 131.4 (d, $^3J_{CP} = 20.6$ Hz, ipso of *p*-tolyl group), 130.8, 130.7, 130.3, 130.2, 120.9 (d, $^1J_{CP} = 104.3$ Hz, ipso of Ph groups), 106.4 (d, $^1J_{PC} = 105.1$ Hz) 39.2 (d, $^3J_{PNC} = 2.9$ Hz), 22.1; ^{31}P NMR (CH_3CN, δ) 45.6.

^{13}C and ^{31}P NMR of One-Pot Reaction Mixtures. These experiments employed Ti-substituted ylide solutions in THF made in the standard fashion from fully labeled $(Me_2N)_3P{=}^{13}CH_2$, $TiCl_3O\textit{i}Pr$, and 4 equiv of $NaN(SiMe_3)_2$, at a total concentration of approximately 0.1 *M*.

NMR Characterization of Reaction Intermediates from Vinylphosphonium Salts (Scheme 5, Figures 3−7). These reactions were carried out either in an inert-atmosphere glovebox or on a Schlenk manifold, with cooling bath temperatures of −60 °C and −78 °C, respectively. Representative procedure: $[(Me_2N)_3P^{13}CH{=}CHC_6H_4CH_3]BPh_4$ (**13a**·BPh_4-$^{13}C_1$, 60 mg, 0.10 mmol) was dissolved in 8−10 mL of THF by vigorous stirring or shaking for several minutes at room temperature. The solution was then cooled for 10 min, during which some of the vinylphosphonium salt reprecipitated as a fine powder and was then treated with a cooled solution of

Table 5. Results of Experiments Described in Scheme 6

reaction	allene resonance	small aldehyde resonance	large aldehyde resonance
16a + **47**	206.87 (**12**)	191.57 (**46**)	190.41 (**47**)
16a + **48**	206.83 (**12**)	191.57 (**46**)	190.72 (**48**)
16b + **46**	206.42 (**19**)	190.50 (**47**)	191.64 (**46**)
16b + **48**	206.34 (**19**)	190.42 (**47**)	190.62 (**48**)
16c + **46**	206.72 (**20**)	190.70 (**48**)	191.60 (**46**)
16c + **47**	206.71 (**20**)	190.64 (**48**)	190.42 (**47**)

PhLi (23 mg of 92% pure solid, 0.25 mmol) in 1 mL of THF, causing a gradual color change to yellow. Inadvertent exposure of this solution to air or moisture results in the immediate loss of the yellow color, with NMR showing the major species to be the starting material. After stirring or standing with occasional stirring for 30 min at low temperature, the yellow solution was then treated with a cooled solution of the appropriate aldehyde (0.40 mmol) in 1 mL of THF, causing a substantial discharge of the yellow color. At each point, aliquots were transferred to cooled screw-cap 5 mm NMR tubes (Wilmad Co.) and kept at −78 °C until they could be examined by low-temperature NMR. Samples were allowed to reach constant temperature by standing for at least 10 min in the cooled NMR probe before data acquisition was started, except for experiments that measured the response of the spectrum to changes in temperature. In these cases, data acquisition was initiated as soon as the probe temperature reached the indicated value. The reported NMR probe temperatures are approximate (±5 °C), as no calibration was performed.

Generation of Allenic Phosphorane 16. In an inert-atmosphere drybox, $[(Me_2N)_3P^{13}CH{=}CHC_6H_4CH_3]BPh_4$ (75 mg, 0.12 mmol) was suspended in a mixture of 5 mL of THF and 0.8 mL of C_6D_6 and chilled to −60 °C. A cooled solution of 2.5 equiv of PhLi (29 mg of 92% pure solid) in THF (2 mL) was added by pipette, and the mixture was allowed to stand for 30 minutes with occasional swirling. Some unreacted vinylphosphonium salt remained suspended in the mixture. A cooled solution of trifluoroacetophenone (167 mg, 0.95 mmol, 8 equiv) in 1 mL of THF was then added. A sample was removed and quickly filtered through a chilled pipette plugged with a glass fiber filter into an NMR tube cooled to −60 °C. ^{13}C NMR and ^{31}P NMR at −60 °C revealed a single product species along with unreacted vinylphosphonium salt and ketone (^{13}C NMR 206.7 ppm), as reported in the text. Resonances for the oxaphosphetane persisted upon warming the NMR sample to room temperature for 1 h. Conversion to allene was observed upon heating the NMR sample in the probe to 50 °C for 1 h.

Oxaphosphetane Crossover Experiments (Scheme 6). In an inert-atmosphere drybox, a solution of **15a**-$^{13}C_1$ (148 mg, 0.25 mmol) in 7.4 mL of THF was cooled to −60 °C. The mixture was treated with a cooled solution of PhLi (44 mg of 92% pure material, 0.48 mmol, 1.9 equiv) in 1.5 mL of THF. After standing with occasional swirling for 30 min, most of the solid was dissolved, forming a yellow solution. The solution was divided into six roughly equal portions using a cold pipette and precooled receiving vials. Two of these vials were treated with a −50 °C solution of 4-methylbenzaldehyde (**46**, 32 mg, 0.27 mmol, ca. 6 equiv each), in 0.7 mL of THF, causing an immediate loss of the yellow color. The other pairs of vials were likewise treated with solutions of 4-methoxybenzaldehyde (**47**, 36 mg, 0.26 mmol) or 3,4,5-trimethoxybenzaldehyde (**48**, 49 mg, 0.25 mmol). After standing for 15 min at −50 °C, approximately 20 equiv (0.83 mmol) of the other two aldehydes were added to each reaction, as shown in Scheme 6, after which the mixtures were allowed to warm to room temperature. Each reaction was then opened to air, subjected to brief rotary evaporation to remove most of the solvent, dissolved in 1 mL of $CDCl_3$, filtered, and analyzed immediately by ^{13}C NMR. The peaks appearing in the downfield portion of each spectrum (including the labeled carbon at the center of each allene unit and the aldehyde carbonyl carbons) are noted in Table 5. Resolution of closely-spaced allene signals (**12** and **20**) was verified by mixing portions of each sample; assignments were confirmed by generation of each ^{13}C-labeled allene using only **16a** and the appropriate aldehyde. Data shown in Scheme 6 was generated using solutions of approximately the same composition as above, with the exception that 10% C_6D_6 was added for spectrometer locking.

Synthesis of 21. 2-Bromobenzaldehyde (2.37 g, 12.8 mmol) was refluxed for 5 h in 85 mL of benzene with (*R,R*)-stilbenediol (2.95, 13.8 mmol, prepared by Sharpless asymmetric dihydroxylation of *trans*-stilbene using AD-mix-β[54] and subsequent recrystallization) and a catalytic amount of *p*-toluenesulfonic acid, using a Dean−Stark trap to remove water. Solvent was removed by rotary evaporation, and the product was purified by flash chromatography (7:3 petroleum ether/methylene chloride) and dried under vacuum to obtain the desired cyclic acetal as a pale yellow, very viscous oil (4.59 g, 12.1 mmol, 94% yield). ^1H NMR ($CDCl_3$, δ) 7.92 (d, $J = 7.8$ Hz, 1H), 7.65 (d, $J = 8.1$ Hz, 1H), 7.48−7.15 (m, 14 H), 6.71 (s, 1H), 5.04 (s, 2H); ^{13}C NMR ($CDCl_3$, δ) 138.8, 137.2, 136.9, 133.6, 131.4, 130.5, 130.4, 129.2, 128.8, 128.2, 127.6, 126.8, 123.7, 104.1, 87.86, 85.9.

Under inert atmosphere, a −78 °C solution of the acetal 4.59 g (12.1 mmol) in 150 mL of dry diethyl ether was treated with *n*-BuLi (6.1 mL of a 2.0 *M* solution, 12.1 mmol). The reaction mixture was warmed to 0 °C for 15 min and then cooled again to −78 °C. To the resulting dark gold solution was added an ether solution of $P(NMe_2)_2Cl$ (1.83 g, 12.0 mmol), in dropwise fashion over approximately 40 min, and the reaction mixture was then allowed to warm slowly to room temperature. The cloudy, colorless reaction mixture was filtered under N_2 and the volume reduced to approximately 10 mL. A large excess of CH_3I (34 g, 240 mmol) in 20 mL of hexane was added and the reaction mixture stored at −30 °C to complete precipitation of the vinylphosphonium salt **21**, which was isolated as a white powder by filtration, washing with hexane, and drying under vacuum (4.05 g, 7.2 mmol, 60%). ^1H NMR ($CDCl_3$, δ) 8.25 (t, $J = 6.9$ Hz, 1H), 7.93 (t, $J = 7.2$ Hz, 1 H), 7.82−7.73 (m, 2H), 7.39−7.29 (m, 10H), 6.60 (s, 1H), 5.18 (d, $J = 4.1$ Hz, 1H), 4.96 (d, $J = 4.1$ Hz, 1H), 2.90 (d, $J = 10.5$ Hz, 9H), 2.77 (d, $J = 10.2$ Hz, 3H), 2.57 (d, $J = 12.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$, δ) 142.5 (d, $J_{PC} = 10.3$ Hz), 136.7, 135.9, 135.4, 134.2, 131.5, 131.3, 130.2, 130.1, 129.4, 129.2, 129.1, 128.9, 127.8, 127.3, 127.6, 126.9, 121.4 (d, $^1J_{PC} = 114.6$ Hz), 100.7 (d, $^3J_{PC} = 3.3$ Hz), 87.2, 85.8, 37.9 (d, $J_{PC} = 3.1$ Hz), 37.8 (d, $J_{PC} = 3.3$ Hz), 13.8 (d, $J_{PC} = 90.9$ Hz); ^{31}P NMR (CD_3CN, δ) 60.1; IR (CH_2Cl_2, cm^{-1}) 3094 (w), 3038, 2957, 1481, 1457, 1301, 1172, 1102, 1066, 996 (s); UV-vis (CH_2Cl_2) 232, 246; $[\alpha]^{298}{}_D + 11.0$ ($c = 1.45$, CH_2Cl_2); mp 158−160 °C.

Synthesis of 22. A solution of (*S*)-(−)-2-bromo-α-methylbenzyl alcohol (3.816 g, 18.99 mmol, Aldrich Chemical Co.) in 35 mL of DMSO was treated with finely powdered KOH (4.2 g, 75 mmol), and the mixture was stirred for 5 min, followed by addition of CH_3I (6.3 g, 44.4 mmol) and stirring for 30 min. A 100 mL volume of Et_2O was added, and the solution was washed with saturated $NaHCO_3$ (3 × 150 mL) followed by brine (1 × 100 mL). The organic layer was dried with $MgSO_4$, filtered, and rotary evaporated to give the methyl ether as a dark-gold oil (3.74 g, 17.4 mmol, 91% yield). ^1H NMR ($CDCl_3$, δ) 7.53 (m, 2H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 4.71 (q, $J = 6.6$ Hz, 1H), 3.26 (s, 3H), 1.40 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, δ) 143.1, 133.1, 129.1, 128.3, 127.4, 123.1, 78.7. 57.2, 23.0.

(*S*)-(−)-2-Bromo-α-methylbenzyl methyl ether (1.517 g, 7.06 mmol in 60 mL of Et_2O), *n*-BuLi (3.55 mL of 2.0 M solution, 7.1 mmol), and $P(Me_2N)_2Cl$ (1.10 g, 7.12 mmol in 20 mL of Et_2O) were combined in a procedure analogous to that described above for **21**. The crude phosphine was isolated as a sticky oil and was redissolved in a minimum amount of ether instead of hexane before treatment with CH_3I (19.8 g, 140 mmol). Hexane was added to encourage precipitation of the

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(54) Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K.-S.; Kwong, H.-L.; Morikawa, K.; Wang, Z.-M.; Xu, D.; Zhang, X.-L. *J. Org. Chem.* **1992**, *57*, 2768−2771.

(55) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

phosphonium salt at −30 °C as above. The phosphonium salt was isolated as a white powder after filtration, washing with hexane, and drying under vacuum (1.905 g, 73%). ^{1}H NMR (CDCl$_3$, δ) 7.73 (br s, 2H), 7.62−7.49 (m, 2H), 4.56 (q, J = 6.0 Hz, 1H), 3.29 (s, 3H), 2.89 (d, $^{3}J_{PH}$ = 4.2 Hz, 6H), 2.92 (d, $^{3}J_{PH}$ = 3.9 Hz, 6H), 2.52 (d, $^{2}J_{PH}$ = 12.9 Hz, 3H), 1.45 (d, J = 6.0 Hz, 3H); ^{13}C NMR (CD$_3$CN, δ) 148.0 (d, $^{2}J_{PC}$ = 11.3 Hz), 134.8, 133.2 (d, $^{2}J_{PC}$ = 11.5 Hz), 128.5 (d, $^{3}J_{PC}$ = 7.0 Hz), 128.3 (d, $^{3}J_{PC}$ = 5.2 Hz), 119.9 (d, $^{1}J_{PC}$ = 115.8 Hz), 74.3 (d, $^{3}J_{PC}$ = 2.8 Hz), 55.4, 36.7 (d, $^{3}J_{PC}$ = 3.3 Hz), 21.6, 12.7 (d, $^{1}J_{PC}$ = 90.9 Hz); ^{31}P NMR (CD$_3$CN, δ) 60.7; IR (CH$_2$Cl$_2$, cm^{-1}) 3033, 2950, 2821, 1477, 1302, 1173, 1110, 1098, 997 (s), 898; UV-vis (CH$_2$Cl$_2$) 230, 248; $[\alpha]^{298}_{D}$ −29.7 (c = 10.7, CH$_2$Cl$_2$); mp 180−182 °C.

Asymmetric Synthesis of Allenes (Scheme 7). Phosphonium salt **21** (0.240 g, 0.427 mmol) was stirred with 1 equiv of NaN(SiMe$_3$)$_2$ (0.386 g of a 1.106 mmol/g of solution in THF) in 30 mL of THF for 10 min. The resulting dark golden-orange ylide solution was added to a solution of TiCl$_3$O*i*Pr (91 mg, 0.43 mmol in 5 mL of hexane), forming a cloudy dark red-orange mixture, which was then treated with equiv of NaN(SiMe$_3$)$_2$ in THF. The metalated ylide mixture was divided into two equal portions, and each was treated with 8.8 equiv of aldehyde (benzaldehyde, 200 mg, 1.89 mmol; 4-methylbenzaldehyde, 230 mg, 1.92 mmol), causing an immediate color change to yellow. After standing overnight, each reaction mixture was reduced by rotary evaporation, and the resulting sticky solid dissolved in a minimal amount of CH$_2$Cl$_2$ for silica gel chromatography (10% CH$_2$Cl$_2$ in petroleum ether) to yield **23** (6.7 mg, 16.3%) and **12** (12.5 mg, 27%), respectively. For **23**, $[\alpha]^{298}_{D}$ −110.4° (c = 0.6, toluene); M^{298}_{D} = −211.9°. Optical purity was determined by comparison with the literature:[20] (211.9/1958) × 100 = 10.8%, enriched in the *R*-isomer as shown in Scheme 7. For **12**, $[\alpha]^{298}_{D}$ −118.2° (c = 1.5, toluene); M^{298}_{D} = 260.0°. If one assumes that the *p*-methyl substituents do not make the optical rotation of **12** significantly different from that of **23**, then the optical purity of **12** is approximately 13%, again favoring the *R* configuration. Phosphonium salt **22** was used in exactly the same procedure, yielding allene **12** in 20% yield with an optical rotation of M^{298}_{D} = −200.0°, indicating an optical purity of approximately 10%, enriched in the *R* enantiomer.

25. Under inert atmosphere, a solution of 2-bromobenzaldehyde (2.9 g, 15.7 mmol) in dry Et$_2$O at −78 °C was treated with methyllithium (11.0 mL, 1.4 mmol/mL; 15.4 mmol) by cannula. The solution foamed vigorously and a light pink color developed. After stirring for 3 min, the reaction mixture was added to a slurry of ice in 1 M HCl. The organic layer was separated, and dried over Na$_2$SO$_4$, and the solvent was removed by rotary evaporation to afford racemic 2-bromo-α-methylbenzyl alcohol (1.91 g, 9.5 mmol, 61%), with the ^{1}H NMR spectrum matching that of the commercially available (*S*)-(−)-enantiomer. Conversion to the methyl ether was accomplished as described above for the synthesis of **22**.

2-Bromo-α-methylbenzyl methyl ether (0.786 g, 3.65 mmol) in 40 mL of anhydrous ether was cooled to −78 °C, treated with 2 equiv of *t*-BuLi (4.0 mL, 1.7 M solution), and stirred for 15 min. To the resulting pale yellow solution was added neat *N*-formylpiperidine (0.712 g, 6.3 mmol) by syringe, and the reaction mixture was allowed to warm to room temperature over 1 h. The reaction was quenched with 75 mL of 3 M HCl and extracted with ether (3 × 75 mL), and the combined organic layers were washed with NaHCO$_3$ (150 mL) and brine (150 mL) before drying over Na$_2$SO$_4$. Rotary evaporation, followed by drying under vacuum, yielded aldehyde **25** as a yellow oil (0.410 g, 2.5 mmol, 68%). ^{1}H NMR (CDCl$_3$, δ) 10.28 (s, 1H), 7.82 (d, J = 7.5, 1H), 7.62−7.59 (m, 2H), 7.43 (t, J = 6.9 Hz, 1H), 5.19 (q, J = 6.6 Hz, 1H), 3.23 (s, 3H), 1.44 (d, J = 6.6 Hz, 3H); ^{13}C NMR (CDCl$_3$, δ) 193.3, 147.0, 134.5, 133.8, 133.4, 127.9, 126.9, 76.2, 57.2, 24.3.

26. To a vigorously stirred solution of *trans*-2-phenyl-1-cyclopropanecarboxylic acid (2.536 g, 15.7 mmol) in 100 mL of THF at 0 °C was added solid LiAlH$_4$ (1.911 g, 48.7 mmol) in small portions over 40 min. The reaction mixture was stirred for 90 min and was then quenched by the cautious addition of water (75 mL), 10% aqueous NaOH (50 mL), and water (75 mL). The mixture was extracted with Et$_2$O (3 × 100 mL), and the combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, and reduced by rotary evaporation to provide *trans*-2-phenyl-1-cyclopropanemethanol (1.96 g, 13.2 mmol, 85%) as a pale yellow oil. ^{1}H NMR (CDCl$_3$, δ) 7.36−7.14 (m, 5H), 3.63 (d, J = 6.6 Hz, 2H), 3.33 (br s, 1H), 1.89−1.84 (m, 1H), 1.54−1.44 (m, 1H), 1.04−0.95 (m, 2H); ^{13}C NMR (CDCl$_3$, δ) 143.2, 128.9, 126.4, 126.1, 66.6, 25.7, 21.8, 14.5. To a stirred slurry of pyridinium chlorochromate (4.23 g, 19.6 mmol) in 150 mL of CH$_2$Cl$_2$ was added *trans*-2-phenyl-1-cyclopropanemethanol (1.96 g, 13.2 mmol) in 10 mL of CH$_2$Cl$_2$. The reaction mixture was stirred for 1 h at room temperature, during which time the color changed to very dark brown and a sticky brown precipitate was observed. The liquid in the flask was decanted and concentrated by rotary evaporation and the resulting crimson oil purified by passage over a short silica column eluting with THF. Evaporation of the solvent provided **26** (1.671 g, 11.44 mmol, 86%) as a colorless crystalline solid. ^{1}H NMR (CDCl$_3$, δ) 9.35 (d, J = 4.5 Hz, 1H), 7.34−7.25 (m, 3H), 7.14 (d, J = 7.2 Hz, 2H), 2.63 (m, 1H), 2.18 (m, 1H), 1.75 (m, 1H), 1.52 (m, 1H); ^{13}C NMR (CDCl$_3$, δ) 200.1, 139.4, 129.0, 127.3, 126.7, 34.2, 27.0, 16.9.

27. *o*-Phthalaldehyde (3.187, 23.78), (*R*,*R*)-(+)-1,2-diphenyl-1,2-ethanediol (stilbenediol, 5.45 g, 25.5 mmol), and a catalytic amount of *p*-toluenesulfonic acid were combined in benzene and heated at reflux using a Dean−Stark trap. After approximately 3 h, the reaction was allowed to cool, washed with water, and dried over Na$_2$SO$_4$. Evaporation of the solvent provided **27** as a viscous yellow oil (6.7 g, 78%), which NMR showed to be the result of clean monoprotection. However, samples of this aldehyde were purified by silica gel chromatography before use. ^{1}H NMR (CDCl$_3$, δ) 8.00 (br d, J = 7.8 Hz, 1H), 7.71 (td, J = 7.5 Hz, 1.5 Hz, 1H), 7.59 (td, J = 7.5, 1.1 Hz, 1H), 7.36−7.31 (m, 11H), 7.07 (s, 1H), 5.04 (d, J = 7.8 Hz, 1H), 4.96 (d, J = 7.8 Hz, 1H); ^{13}C NMR, (CDCl$_3$, δ) 192.3, 139.8, 138.4, 136.6, 134.9, 134.4, 131.0, 130.1, 129.2, 128.9, 127.4, 126.9. 102.0, 87.9, 85.8.

General Procedure for Observation of Oxaphosphetane Diastereomers (Figure 8). A solution of [(Me$_2$N)$_3$P^{13}CH=CH-C$_6$H$_4$CH$_3$]BPh$_4$ (**13a**) in THF was treated with 2 equiv of phenyllithium at −78 °C. To the solution of deprotonated vinylphosphonium was added the desired aldehyde as a chilled (−78 °C) solution in THF. Upon addition of the aldehyde, an immediate color change from yellow to colorless was observed. Aliquots of this solution were transferred by cannula into cold (liquid N$_2$ chilled) screw-cap NMR tubes under positive N$_2$ pressure, which were stored at −78 °C for up to 2 h before low-temperature NMR analysis. In general, diastereomers were more distinguishable by ^{13}C NMR than by ^{31}P NMR. For the oxaphosphetane **28** derived from **25**: ^{13}C NMR (THF, δ) 155.0 (d, $^{1}J_{CP}$ = 163.5 Hz), 154.2 (d, $^{1}J_{CP}$ = 160.2 Hz). For the oxaphosphetane derived from **26**: ^{13}C NMR (THF, δ) 156.6 (d, $^{1}J_{CP}$ = 157.7 Hz), 155.8 (d, $^{1}J_{CP}$ = 157.6 Hz); ^{31}P NMR (THF, δ) −18.8 (d, $^{1}J_{CP}$ = 158.50 Hz), 19.3 (d, $^{1}J_{CP}$ = 154.3 Hz); for the oxaphosphetane derived from **27**: ^{13}C NMR (THF, δ) 154.7 (d, $^{1}J_{CP}$ = 164.0 Hz), 154.2 (d, $^{1}J_{CP}$ = 160.4 Hz); ^{31}P NMR (THF, δ) −17.7 (d, $^{1}J_{CP}$ = 151.5 Hz), −18.0 (d, $^{1}J_{CP}$ = 167.4 Hz).

The NMR tubes were warmed to 25 °C and allowed to stand for several hours before diastereomer ratios were obtained by ^{13}C NMR of the central (labeled) allene carbon. In the case of the allene derived from **27**, these ^{13}C peaks were found to be coincident, so the allene was isolated and the diastereomer ratio determined by comparison of other resonances (see below). The solutions from which the NMR aliquots were removed were allowed to warm to room temperature overnight. The solvent was removed by rotary evaporation and the residue purified by flash chromatography, taking care to avoid separation of diastereomers, to provide the allenes described below.

30. From vinylphosphonium salt **13a**-^{13}C$_1$ (0.109 g, 0.182 mmol), PhLi (40 mg, 0.48 mmol), and aldehyde **25** (0.166 g, 1.01 mmol), allene **30** was isolated (27 mg, 0.102 mmol, 56%) as a mixture of diastereomers. ^{1}H NMR (CDCl$_3$, δ, asterisks mark resonances of the major diastereomer): 7.46−7.41 (m, 2H), 7.27−7.20 (m, 3H), 7.14 (d, J = 7.5 Hz, 2H), *6.94 (d, J = 6.6 Hz, 1H), 6.93 (d, J = 6.3 Hz, 1H) 6.55 (m, uneven triplet), overlapping doublets, 2H), 4.53−4.44 (m, 2 overlapping diastereotopic quartets, 1H), *3.29 (s, 3H), 3.27 (s, 3H), 2.35 (s, 3H), 1.48 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (CDCl$_3$, δ) 208.31, 208.17, 137.55, 129.9, 128.7, 128.6, 127.8.0, 127.8, 127.5, 126.8, *98.0, 97.8, 95.4, *95.3, *77.4, 77.3, 57.0, *23.7, 21.6. HPLC (5 μm silica column, 15 cm, ES Industries, 0.5% 2-propanol in hexanes) showed a diastereomer ratio of 2.4:1 for the isolated allene, in close agreement with the ratio of 2.5:1 obtained by NMR of the unchromatographed reaction mixture.

31. From vinylphosphonium salt **13a**-^{13}C$_1$ (0.112 g, 0.187 mmol), PhLi (40 mg, 0.48 mmol), and aldehyde **26** (0.150 g, 1.06 mmol) was isolated allene **31** as an equal mixture of diastereomers. ^{1}H NMR (C$_6$D$_6$, δ) 7.18−6.82 (m, 9H), 6.20 (d, $J = 6.0$ Hz, 1H), 5.42 (t, $J = 6.3$ Hz, 1H), 2.35 (s, 3H), 1.85−1.79 (m, 1H), 1.46−1.39 (m, 1H), 0.95−0.90 (m, 2H); ^{13}C NMR (C$_6$D$_6$, δ) 204.42, 204.19, 128.8, 127.7, 126.9, 126.6, 125.3, 125.1, 97.6, 96.4, 25.3, 20.8, 20.3, 16.4; UV-vis (CH$_2$Cl$_2$) 232, 254 (br sh).

32. From vinylphosphonium salt **13a**-^{13}C$_1$ (0.101 g, 0.168 mmol), PhLi (40 mg, 0.48 mmol), and aldehyde **27** (0.215 g, 0.70 mmol), was isolated allene **32** as a diastereomeric mixture. A diastereomer ratio of 1.7:1 was determined by comparing the intensities of the indicated ^{13}C peaks (* = major isomer; ** = minor isomer). ^{1}H NMR (CDCl$_3$, δ) 7.87−7.84 (m, 1H), 7.56−7.52 (m, 1H), 7.24−7.25 (m, 10H), 7.13−7.12 (m, 2H), 6.72 (s, 1H), 6.71 (d, $J = 7.5$ Hz), 6.61−6.58 (m, 1H - diastereomers), 4.98 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (CDCl$_3$, δ) 208.9, 137.8, 136.7, 136.0, 133.7, 132.0, 130.0, 129.0, 128.9, 128.1, 127.7, 126.8, 126.5, 126.4, 126.2, 125.9, **102.2, *102.1, **97.3, *97.2, 94.6, *86.9, **86.8, 84.7, 20.8; $[\alpha]^{298}{}_{D} = +67.0$ ($c = 1.9$, CH$_2$Cl$_2$).

(±)-29. (Me$_2$N)$_3$P═CH$_2$ (0.100 g, 0.565 mmol) was added to a solution of TiCl$_2$(O*i*Pr)$_2$ (0.133 g, 0.564 mmol) in 5 mL of THF. To the resulting bright orange solution was added NaN(SiMe$_3$)$_2$ (0.510 g of 1.106 mmol/g solution in THF, 0.565 mmol). After approximately 1 m, racemic aldehyde **25** (0.234 g, 1.43 mmol, 2.5 equiv) was added, causing the opaque dark red-brown solution to become light orange-yellow with a white precipitate. The reaction was allowed to stand for 2 h and then filtered over a medium frit and the solid rinsed with hexane and dried briefly in vacuo before being brought out of the drybox. NMR of the crude material in D$_2$O showed a clean compound. The solid was dissolved in H$_2$O, filtered through a medium frit, and treated with aqueous NaBPh$_4$ (0.200 g, 0.59 mmol), resulting in a milky white precipitate. Saturated brine (15 mL) was added to facilitate precipitation, and the mixture was filtered, rinsed with water (5 × 25 mL), and dried under vacuum for 48 h. ^{1}H NMR (D$_2$O, δ) 7.92 (dd, $J = 17.4$ Hz, $^3J_{PH} = 22.8$ Hz, 1H), 7.78 (d, $J = 7.5$ Hz, 1H), 7.56−7.43 (m, 3H), 6.68 (dd, $J = 7.4$ Hz, $^2J_{PH} = 23.7$ Hz, 1H), ∼4.78 (should be a quartet, obscured by HOD peak), 3.25 (s, 3H), 2.81 (d, $^3J_{PC} = 9.6$ Hz, 18H), 1.48 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (D$_2$O, δ) 149.1 (d, $^2J_{PC} = 7.6$ Hz), 131.7, 128.9, 128.2, 127.9, 111.9 (d, $^1J_{PC} = 159.7$ Hz), 78.8, 56.1, 36.5 (d, $^2J_{PC} = 3.6$ Hz), 22.2; ^{31}P NMR (CD$_3$CN, δ) 51.3; IR (CH$_2$Cl$_2$, cm^{-1}) 3059, 3005, 2996, 2938, 2905, 2821, 1611, 1594, 1582, 1482, 1181, 1110, 1006 (s), 864. Use of enantiomerically pure (*S*)-**25** (derived from commercially available (*S*)-(−)−2-bromo-α-methylbenzyl alcohol) provides **29·**BPh$_4$ with $[\alpha]^{298}{}_{D}$ +22.8 ($c = 0.80$, CH$_3$CN).

Allene 30 from 29. Vinylphosphonium salt **29** (0.104 g, 0.161 mmol) in 15 mL of THF was treated with PhLi (0.028 g, 0.33 mmol, dissolved in 1 mL of THF) at −78 °C via cannula. After stirring for 10 min, a large excess of *p*-tolualdehyde (0.5 g, 4.2 mmol) was added with rapid stirring. The cold bath was removed, and the reaction mixture was allowed to warm to room temperature for 5 h. After rotary evaporation to a sticky solid, flash chromatography over silica gel (10% EtOAc in petroleum ether) provided mixed fractions containing aldehyde and allene. More careful separation was not attempted so as to avoid enriching the mixture in one allene diastereomer. Because this allene was not prepared with ^{13}C-labeled methylide, the diastereomeric ratio could not be determined by ^{13}C NMR of the product mixture. Instead, the diastereomeric ratio was determined to be 1:1 by comparison of the heights of the OMe peaks in the ^{1}H NMR spectrum, since *p*-tolualdehyde does not obscure these resonances.

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Supporting Information Available: NMR spectra of adduct **1** + 4 NaN(SiMe$_3$)$_2$ and of intermediate species under one-pot reaction conditions and of Ph$_{3-n}$(Me$_2$N)$_n$P-containing methylphosphonium iodides and methylides **13b**−**d**, **22**, **25**, **27**, **29**, and **30**−**32** (29 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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