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Synthesis of the first metal-free phosphanylphosphonate and its use in the "phospha-Wittig-Horner" Reaction

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The synthesis of the first phophanylphosphonate, Mes*PH-PO(OEt)$_2$ (**2-H**), in which the P(III) centre is not coordinated by a M(CO)$_5$ (M = W, Mo, Cr) fragment is reported. The title compound reacts with LDA under the formation of **2-Li** which is best described as the enolate form with a high double bond character between the two phosphorus centres. **2-Li** is shown to engage In the phospha-Wittig-Horner reaction and converts aldehydes into phosphaalkenes that are metal-free and thus available for future manipulations at the phophorus lone pair. Using a selection of aldehydes with aliphatic, aromatic or vinylic substituents as substrates, phosphaalkene formation proceeds in high yields and high *E*-selectivity. The selectivity is however compromised during purification on standard silica which was found to promote *E/Z* isomerization.

Introduction

Conjugated organic molecules are attractive building blocks for the assembly of elaborate architectures that can be applied in the field of organic electronics. Carbon-rich, π-conjugated scaffolds have been widely used in the fabrication of organic light emitting diodes (OLEDs),[1,2] molecular wires,[3] non-linear optics,[4] dye-sensitized solar cells (DSCs),[5] *etc*. Beyond modifications exclusively at the carbon backbone, the incorporation of other main group elements, in particular phosphorus, into such conjugated structures has provided additional means to tune the electronic properties of the compounds.[6–12] In this context, phosphaalkenes as a heavier analogue to olefins have attracted growing attention over the past years due to their opto-electronic properties and intriguing coordination chemistry.[13]

Since their first report by Becker in 1976,[14] numerous synthetic pathways to phosphaalkenes have been reported.[15–28] In analogy to the Wittig reaction that uses phosphorus ylides, RC=PR$_3$, to convert carbonyl compounds into alkenes and the Horner-Wadsworth-Emmons (HWE) reaction based on RCH$_2$P(=O)(OR)$_2$, corresponding phosphorus analogous reagents have been developed. In the late 1980s, Mathey and colleagues reported the so-called "phospha-Wittig-Horner" reaction, *i.e.* the phosphorus analogue of the HWE reaction that converts carbonyl compounds into phosphaalkenes.[29,30] The reagents that are used for this purpose are phosphanylphosphonates in which the RCH$_2$ group of the HWE reagent is replaced by an isolobal RPH fragment. In these early reports, metal carbonyls, most frequently tungsten or molybdenum pentacarbonyl, were coordinated to the phosphorus lone pair of the phosphanylphosphonates to stabilize the reagent itself, but also of the formed phosphaalkene products. Ourselves, we have recently reported a reliable synthetic protocol for the multi-gram preparation of transition metal-coordinated phosphanylphosphonates,[31] and proposed a mechanism for the phospha-Wittig-Horner reaction using these substrates.[32]

In 1998, Protasiewicz *et al.* reported the first phosphinylidene-λ^4-phosphoranes, RP=PMe$_3$ (R = 2,6-dimesitylphenyl (Dmp) or 2,4,6-^{t}Bu$_3$Ph (Mes*)), as true phosphorus analogues of the original Wittig-type RC=PR$_3$ ylide. The two compounds are not only isolobal, but also show analogous reactivity when exposed to aldehydes, with the Mes*P=PMe$_3$ reacting under the formation of phosphaalkenes.[33–36] An interesting aspect of the described reagents is the fact that they are stable (days to week in solution)[37] without the necessity to have the phosphorus lone pair coordinated to metal fragments. It is shown that bulky substituents at the low-valent phosphorus centre can provide sufficient kinetic stabilization to allow isolation of the reagent as well as of the phosphaalkene product. Omitting metal fragments has the advantage that products that are generated from these reagents can be further manipulated by modifications of the P(III) centre without the need for tedious removal of the metal.

In view of the successful kinetic stabilization of phosphinylidene-λ^4-phosphoranes, and low-valent phosphorus compounds in general by bulky substituents,[38] we were intrigued by the possibility to implement such a strategy also for phosphanylphosphonates which had previously only been described as their M(CO)$_5$ complexes (Figure 1). Metal-free phosphanylphosphonates would not only provide a new access to phosphaalkenes, but also other compounds such as oxaphospholes and ethenyl-bridged bis-phospholes that we made recently accessible from metal-coordinated phosphanylphosphonates.[39] With this in mind, the ambition of the work described herein is to broaden the toolbox for uncoordinated phosphaalkene synthesis by developing metal-free phosphanylphosphonates and to explore their scope in the phospha-Wittig-Horner reaction.

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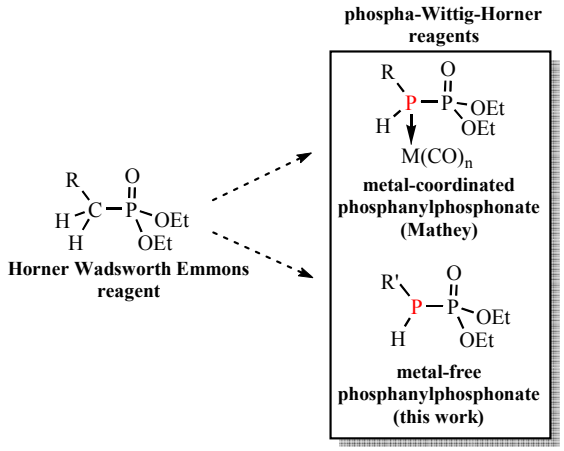
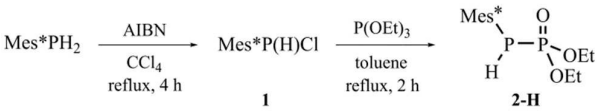


Figure 1. Evolution of the Horner-Wadsworth-Emmons (HWE) reaction to its phosphorus analogue, the "phospha-Wittig-Horner" reaction. A sufficiently bulky substituent R' such as $^{t}Bu_3Ph$ (Mes*) should eliminate the necessity for a transition metal at the P(III) centre and facilitate the isolation of metal-free phosphanylphosphonates.

Results & Discussion

From the variety of different bulky groups that have been reported for kinetic stabilization of thermally labile phosphorus compounds (Mes, Dmp, adamantyl), we decided to target metal-free phosphanylphosphonates with a Mes* group at the P(III) centre. The synthetic sequence towards the title compound is outlined in Scheme 1, and commences with Mes^*PH_2 that is accessible in high yields following known procedures.[40,41] Chlorination of Mes^*PH_2 by CCl_4 in the presence of AIBN affords Mes*P(H)Cl **1** which features a doublet at δ = 20.7 ppm in its ^{31}P NMR (C_6D_6) spectrum with a coupling constant of $^{1}J_{P\text{-}H}$ = 211 Hz.[42,43] Phosphane **1** was used in the next step without further purification and treated with triethyl phosphite in a phospha-Michael-Arbuzov reaction to afford the desired phospha-Wittig-Horner reagent **2-H** in good overall yields.



Scheme 1. Synthesis of the phosphanylphosphonate **2-H**, the phospha-Wittig-Horner reagent.

The ^{31}P NMR spectrum of phosphanylphosphonate **2-H** exhibits two doublets at δ = 35.0 and -88.8 ppm with a $^{1}J_{P\text{-}P}$ of 222 Hz. Compound **2-H** is stable under ambient conditions and can be stored in the freezer at -20°C for months. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a pentane solution. Phosphanylphosphonate **2-H** crystalizes in the triclinic space group P-1 as colourless blocks. The solid state structure (Figure 2) shows the expected P1-P2 (2.1854(7) Å) distance but slightly elongated C1-P1 (1.8539(19) Å) distances compared to those of other phosphanylphosphonates which are coordinated to a tungsten pentacarbonyl fragment. Compound **2-H** also shows a relatively small C1-P1-P2 angle with 96.57(6)° compared to 102.1-104.7° in the transition metal-coordinated phosphanylphosphonates.[31,44] Interestingly, the P1 atom is highly pyramidalized (Σ_{angles} = 284.8°).

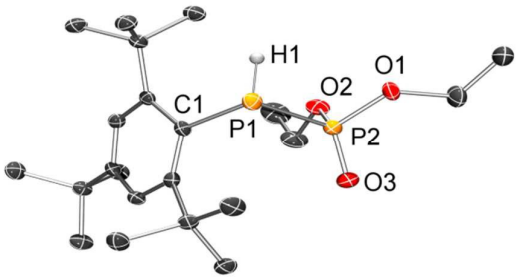


Figure 2. ORTEP drawing of **2-H** at 30% probability ellipsoids. Hydrogen atoms except the P-bound H1 are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-P1 1.8539(19), P1-P2 2.1854(7), P2-O1 1.5770(14), P2-O2 1.5877(13), P2-O3 1.4716(13). C1-P1-P2: 96.57(6).

As the phospha-Wittig-Horner reaction is initiated by deprotonation of the P(III) centre, the reaction of **2-H** with LDA was examined in more detail. The formation of **2-Li** is accompanied by a characteristic colour change of the solution from colourless to bright yellow, and is complete at -50 °C within seconds. The ^{31}P NMR spectrum of **2-Li** is distinctly different to that of **2-H** (Figure 3), with the Δδ between the resonances of the P(III) and P(V) centres having increased significantly in **2-Li**. In addition, the $^{1}J_{P\text{-}P}$ coupling constant increases from 222 Hz in **2-H** to 615 Hz in **2-Li**. The coupling constant in **2-Li** is thus in the same range as those of phosphanylidene-σ^4-phosphorane,[33] indicating that **2-Li** is best described as the enolate form with a high double bond character between the two phosphorus centres. Interesting to note is that the $^{1}J_{P\text{-}P}$ coupling constant in **2-Li** is also significantly larger than that of the corresponding W- and Mo-coordinated analogues ($^{1}J_{P\text{-}P}$ = 383 and 393 Hz, respectively),[30] pointing towards a decreased bond order in the latter probably due to π-backbonding from the transition metal into the P=P π* orbital. Additionally, the metal coordination may disable the lone pair contribution to negative hyperconjugation that could also explain the decreased bond order.

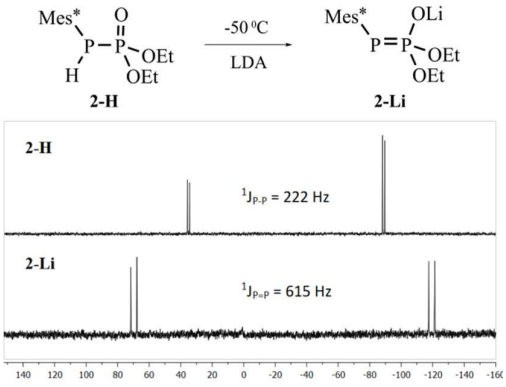
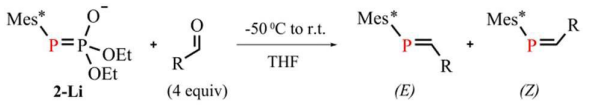


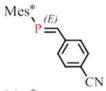
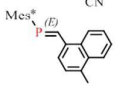
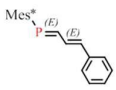
Figure 3. Deprotonation of **2-H** and its significant impact on the chemical shifts and coupling constant (*J*).

A diverse range of aldehydes with aliphatic, aromatic, heterocyclic and vinylic substituents was chosen as substrates for the reaction with the lithiated phospha-Wittig-Horner

reagent **2-Li** (Table 1). Most gratifyingly, the reactions proceeded smoothly and metal-free phosphaalkenes could be isolated in generally good yields, in some instances as a mixture of *E* and *Z* isomers. In analogy to previous reports,[30,33,45] *E*-phosphaalkenes are formed as the major isomers in all cases. For some products, however, significant amounts of the *Z* isomer were formed during the work-up and purification procedures. As discussed in a recent paper,[46] *E/Z* isomerization can be induced by a variety of factors including the chromatographic stationary phase, light, or an acidic environment. In case of the phosphaalkenes described herein, isomerization occurred predominantly during column chromatographic purification on acidic silica.

Table 1. Substrate scope for the transition metal-free phospha-Wittig-Horner reaction.[a]



Aldehyde	Time [h]	Conversion [%][b]	*E*-Phosphaalkene	No.	*E*/*Z*[c]	$^2J_{H-P}$ [Hz] *E*	$^2J_{H-P}$ [Hz] *Z*	Yield [%][d]
	40	64		**3**	99:1	26.0	–	49
	16	100		**4**	84:16	25.0	37.0	71
	16	91		**5**	87:13	25.4	35.7	70
	16	89		**6**	92:8	24.0	35.3	65
	16	72		**7**	81:19	24.1	37.8	40

[a] Reaction conditions: LDA (1.1 eq) for the deprotonation of **2-H** to **2-Li**, aldehyde (4 eq), -50 °C to r.t. [b] Based on the ^{1}H NMR of the crude mixture after the work-up. [c] Isomeric ratio before purification by column or oxalyl chloride treatment. [d] Yield of isolated product(s).

The reaction of **2-Li** with isobutyraldehyde, *i.e.* a representative aliphatic aldehyde, affords the corresponding phosphaalkene *E*-**3** as the only isomer, even after purification by column chromatography. The observed stability towards *E/Z* isomerization is in contrast to all other phosphaalkenes described below, and most likely arises from the bulkiness if the isopropyl substituent which would inflict severe steric congestion with the Mes* group if the compound was in its *Z* isomer form.

The conversion of 4-cyanobenzaldehyde, 4-methyl-1-naphtaldehyde and 2-thiophenecarboxaldehyde leads to the corresponding *E*-phosphaalkenes *E*-**4**,[47] *E*-**5** and *E*-**6**[48] as the major isomers. Longer reaction times do not result in improved overall yields, but give rise to the formation of the *Z* isomers already in the reaction mixtures. Compounds *E*-**4**-**6** are generally characterized by ^{31}P NMR chemical shifts (δ = 283.9, 258.9 and 246.8 ppm for *E*-**4**-**6**, respectively) that are shifted downfield compared to those of *Z*-**4**-**6** ($\Delta\delta$ = 19, 16, and 22 ppm, respectively). The *E*-phosphaalkenes also show smaller $^2J_{H-P}$ coupling constants in their ^{1}H NMR spectra (between 24.0 and 26.0 Hz) compared to those in the *Z*-isomers (between 35.3 and 37.8 Hz). While the *E* isomers are obtained preferentially from the reaction, isomerization to the *Z* isomers is promoted by column chromatography on acidic silica. Leaving solutions of the products under ambient conditions for few days had a similar effect indicating that heat or light also causes *E/Z* isomerization, however the isomerization is accelerated on silica. This effect is representatively demonstrated for compound **4** (see ESI).

Yellow crystals of *Z*-**5** suitable for single crystal X-ray diffraction could be grown by slow evaporation of DCM/acetonitrile solutions. The solid state structure shows the *Z* relationship between the Mes* group and the naphthyl substituent, and is one of few crystal structures of uncoordinated acyclic *Z*-phosphaalkenes (of the type ArP=C(H)R) in the literature.[35,49–56]

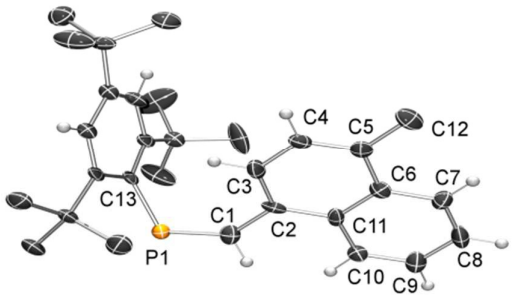


Figure 4. ORTEP plots (50% probability ellipsoids) of *Z*-**5**. Only one of the two independent molecules is shown. Aliphatic hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for the molecule containing P1 and the corresponding values for P2 in square brackets[]: P1-C1 1.663(4) [1.670(5)], P1-C13 1.835(4) [1.854(4)], C13-P1-C1 107.4(2) [107.2(2)], C13-P1-C1-C2 1.9(5) [0.8(6)].

As seen in Figure 4, H_{C3} is located *above* the Mes* group and is therefore expected to be highly shielded due to the strong anisotropic effect induced by this ring. The characteristic upfield signal (doublet of doublets, 5.74 ppm) in the ^{1}H NMR spectrum is a clear-cut proof supporting this claim. A similar, but slightly smaller effect is observed for H_{C4} which shows an upfield resonance (doublet) in the ^{1}H NMR spectrum at 6.68 ppm. Interestingly, the ^{1}H NMR chemical shifts of the two protons are similar to those of the corresponding protons in *Z*-**4**, thus confirming the assignment of the two different isomers also in case of **4**.

Finally, a solution of *trans*-cinnamaldehyde and **2-H** were treated with LDA to afford the vinylic phosphaalkene **7**, a close analogue of which was previously synthesized in our group following a different approach.[57] Purification of *E*-**7** using the methods that were found viable for **3**-**6** did not work in case of **7**, and the overall isolated yield was very low. Gilheany *et al.*[46] recently reported a chromatography-free purification method for the standard Wittig reactions using oxalyl chloride to remove high-valent phosphorus by-products. Inspired by these results, we decided to investigate the suitability of this method also for the purification of *phosphaalkenes*. The hope was that oxalyl chloride reacts with the (P=O)-containing species and leaves the P=C bond in phosphaalkenes intact. Fortunately, this proved to be the case, and no reaction of **7** with oxalyl chloride could be detected, while the (P=O)-containing impurities were further oxidized and could finally be removed by an aqueous work-up. As a result, purification by column chromatography was no longer necessary, and the phosphaalkene can be purified by

recrystallization. The new work-up procedure has the additional advantage that the *E/Z* isomerization that usually occurs on silica can be avoided, and *E*-**7** was obtained as a pure isomer in acceptable isolated yield.

Conclusion

In summary, we have developed a synthetic approach for the multi-gram preparation of phosphanylphosphonate **2-H**. Compound **2-H** lacks a metal fragment coordinated to the P(III) centre, and is kinetically stabilized by a bulky Mes* group instead. The title compound **2-H** has been used as a phospha-Wittig-Horner reagent to convert aldehydes into phosphaalkenes. Using a selection of aldehydes with aliphatic, aromatic or vinylic substituents as substrates, phosphaalkenes were formed in all cases in good overall yields. The reactions show high *E* selectivity, which is however compromised during purification on standard acidic silica which was found to promote *E/Z* isomerization. For more fragile products as in case of the 1-phosphabutadiene **7**, an alternative purification procedure was developed to remove high-valent phosphorus by-products, and that allows purification of the phosphaalkene by recrystallization. The latter method is also preferable over chromatographic purification as it does not promote *E/Z* isomerization.

Acknowledgements

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Experimental details

All reactions were carried out under an inert atmosphere of argon using Schlenk techniques. THF was freshly distilled over Na/benzophenone under nitrogen and glassware was dried thoroughly prior to use. NMR spectra were recorded on a JOEL Eclipse 400 MHz spectrometer. NMR chemical shifts are reported in ppm and coupling constants (*J*) in Hz. ^{1}H NMR and ^{13}C NMR chemical shifts are referenced to the residual solvent signal and ^{31}P NMR spectra externally to 85% $H_3PO_{4(aq)}$.

{Mes*P(H)-P(O)(OEt)$_2$} (2-H) – The residue from the previous step was dissolved in toluene (35 mL) followed by the addition of triethyl phosphite (26.9 mmol, 4.7 mL). The solution was then stirred under reflux for 2 h after which the reaction progress was observed by ^{31}P NMR showing a complete conversion. The volatiles were removed under vacuum using a cold trap. Residue was dissolved in Et_2O, washed with water and brine and dried over $MgSO_4$. Recrystallization from a heptane solution furnished the pure product as white crystals. Yield: 6.9 g, 68%. ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 7.39 (s, 2H), 5.40 (dd, $^{1}J_{H\text{-}P}$ = 231.0 Hz, $^{2}J_{H\text{-}P}$ = 14.2 Hz), 3.82-3.61 (m, 2H), 3.54-3.40 (m, 2H), 1.58 (br s, coalescence, 18H), 1.29 (s, 9H), 1.12-1.03 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 156.7 (coalescence), 150.4 (d, $J_{C\text{-}P}$ = 5.3 Hz), 122.6 (coalescence), 120.7 (dd, $J_{C\text{-}P}$ = 31.2, 11.3 Hz), 61.8 (dd, $J_{C\text{-}P}$ = 7.7, 0.5 Hz), 61.7 (dd, $J_{C\text{-}P}$ = 7.2, 2.1 Hz), 35.0 (d, $J_{C\text{-}P}$ = 1.5 Hz), 33.9 (coalescence), 31.8, 31.4 (d, $J_{C\text{-}P}$ = 1.39 Hz), 16.5 (d, $J_{C\text{-}P}$ = 6.3 Hz), 16.4 (d, $J_{C\text{-}P}$ = 6.4 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 35.0 (d, $^{1}J_{P\text{-}P}$ = 222 Hz), -88.8 (d). Anal. Calcd for $C_{22}H_{40}O_3P_2$: C, 63.75; H, 9.73. Found: C, 63.82; H, 9.57.

General procedure for the phospha-Wittig-Horner reaction – To a solution of the phosphanylphosphonate reagent in THF was added LDA (1.1 eq) at -50 °C, turning the solution into a bright yellow color. A solution of aldehyde (4 eq) in THF was added slowly and the reaction mixture was allowed to reach r.t. and stir for the times mentioned in Table 1. The reaction was then quenched with a satd. solution of $NH_4Cl_{(aq)}$. Solvent was removed under vacuum and the residue redissolved in Et_2O and washed with the same aqueous solution. The solution was dried over $MgSO_4$ and filtered off and the volatiles were removed with rotary evaporator. The crude mixture was then purified either by column chromatography (silica gel) or oxalyl chloride treatment to give the isolated phosphaalkene as a single isomer or mixture of isomers.

***(E)*-(2-methylpropylidene)(2,4,6-tri-tert-butylphenyl)phosphine (*E*-3) –** pWH reagent (0.41 mmol, 170 mg) and isobutyraldehyde were exposed to the reaction conditions to give a crude mixture (215 mg). Column chromatography (pure heptane) afforded the product as white solid. Yield: 42 mg, 49%. ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 7.41 (dd, $^{2}J_{H\text{-}P}$ = 26.0 Hz, $^{3}J_{H\text{-}H}$ = 9.1 Hz, 1H, P=C*H*), 7.39 (s, 2H), 2.85 (m, 1H), 1.51 (s, 18H), 1.33 (s, 9H), 1.12 (d, $^{3}J_{H\text{-}H}$ = 6.6 Hz, 6H). ^{13}C NMR {^{1}H} ($CDCl_3$, 100.5 MHz): δ 187.6 (d, $^{1}J_{C\text{-}P}$ = 37.9 Hz, P=*C*), 153.7 (d, $J_{C\text{-}P}$ = 1.8 Hz), 149.1, 140.0 (d, $^{1}J_{C\text{-}P}$ = 56.1 Hz, *ipso*-Ar*C*), 121.7 (d, $J_{C\text{-}P}$ = 1.2 Hz), 38.4, 35.1 (d, $^{2}J_{C\text{-}P}$ = 24.2 Hz, Isopropyl-*C*H), 35.0, 33.9 (d, $J_{C\text{-}P}$ = 7.6 Hz), 31.5, 23.5 (d, $^{3}J_{C\text{-}P}$ = 15.5 Hz, Isopropyl-*C*H$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 242.1. Anal. Calcd for $C_{22}H_{37}P$: C, 79.47; H, 11.22. Found: C, 78.91; H, 11.26.

***(E)*-((4-methylnaphthalen-1-yl)methylene)(2,4,6-tri-tert-butylphenyl)phosphine (*E*-5) –** The reaction of the pWH-reagent (0.41 mmol, 170 mg) with 4-methyl-1-naphtaldehyde gave a crude mixture which was purified by column chromatography (toluene/heptane, 3:7) to afford mixture of isomers. A second column chromatography (pure heptane) was used in order to separate the isomers *E*-**5** and *Z*-**5** from each other, which yielded the isomers but with small amounts of the other isomer as impurity in each case. Yield: 112 mg, 70%. ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 8.93 (d, $^{2}J_{H\text{-}P}$ = 25.4 Hz, 1H, P=C*H*), 8.02-7.94 (m, 3H), 7.55-7.45 (m, 4H), 7.34 (d, $J_{H\text{-}P}$ = 7.3 Hz, 1H), 2.70 (d, $^{4}J_{H\text{-}H}$ = 1.8 Hz, 3H, Naphtyl-C*H*$_3$), 1.58 (s, 18H), 1.39 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 173.0 (d, $^{1}J_{C\text{-}P}$ = 34.9 Hz, P=*C*), 154.26, 149.85, 139.7 (d, $^{1}J_{C\text{-}P}$ = 54.6 Hz, *ipso*-Ar*C*), 135.8 (d, $J_{C\text{-}P}$ = 13.6 Hz), 135.3 (d, $J_{C\text{-}P}$ = 6.4 Hz), 133.0 , 130.3 (d, $J_{C\text{-}P}$ = 10.8 Hz), 127.0 (d, $J_{C\text{-}P}$ = 3.3 Hz), 125.9 (d, $J_{C\text{-}P}$ = 3.4 Hz), 125.9, 124.9, 124.8 (d, $J_{C\text{-}P}$ = 1.1 Hz), 123.1 (d, $J_{C\text{-}P}$ = 27.2 Hz), 122.0 (d, $J_{C\text{-}P}$ = 0.9 Hz), 38.5, 35.2, 34.1 (d, $J_{C\text{-}P}$ = 7.1 Hz), 31.6, 19.9 (s, Naphtyl-*C*H$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 258.9 (s).

***(Z)*-((4-methylnaphthalen-1-yl)methylene)(2,4,6-tri-tert-butylphenyl)phosphine (*Z*-5) -** ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 8.60 (d, $^{2}J_{H\text{-}P}$ = 35.5 Hz, 1H, P=C*H*), 8.20 (d, $J_{H\text{-}P}$ = 8.6 Hz, 1H), 7.91 (d, $J_{H\text{-}P}$ = 8.2 Hz, 1H), 7.51-7.42 (m, 4H), 6.68 (d, $^{3}J_{H\text{-}H}$ = 7.7 Hz, 1H), 5.74 (dd, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}P}$ = 3.6 Hz, 1H), 2.53 (d, $^{4}J_{H\text{-}H}$ = 2.0 Hz, 3H, Naphtyl-C*H*$_3$), 1.45 (s, 18H), 1.40 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 157.2 (d, $^{1}J_{C\text{-}P}$ = 49.1 Hz, P=*C*), 154.1 (d, $J_{C\text{-}P}$ = 1.4 Hz), 150.9, 134.5 (d, $J_{C\text{-}P}$ = 6.9 Hz), 133.1 (d, $J_{C\text{-}P}$ = 25.9 Hz), 132.7 (d, $J_{C\text{-}P}$ = 3.2 Hz), 130.6, 130.5, 127.7 (d, $J_{C\text{-}P}$ = 11.7 Hz), 126.4 (d, $J_{C\text{-}P}$ = 4.2 Hz), 125.9 (d, $J_{C\text{-}P}$ = 1.5 Hz), 125.3 (d, $J_{C\text{-}P}$ = 0.9 Hz), 124.7 (d, $J_{C\text{-}P}$ = 1.3 Hz), 123.9, 122.5, 38.2, 35.2, 32.7 (d, $J_{C\text{-}P}$ = 7.4 Hz), 31.6, 19.8 (s, Naphtyl-*C*H$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 243.1 (s).

***(E)*-(*(E)*-3-phenylallylidene)(2,4,6-tri-tert-butylphenyl)-phosphine (*E*-7) –** pWH reagent (0.35 mmol, 145 mg) and *trans*-cinnamaldehyde were exposed to the reaction conditions to give a crude from which a major part of the aldehyde was removed by a cold acetonitrile wash. Oxalyl chloride was then added to remove most of the unreacted pWH reagent and the phosphine oxide generated in the reaction. Slow evaporation from a DCM/acetonitrile solution afforded the re-crystallized phosphaalkene *E*-**7** as yellow solid. Yield: 40 mg, 40%. ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 7.95 (dd, $^{2}J_{H\text{-}P}$ = 24.1 Hz, $^{3}J_{H\text{-}H}$ = 13.0 Hz, 1H, P=C*H*), 7.52-7.33 (m, 6H), 7.33-7.28 (t, *J* = 7.6 Hz, 2H), 7.24-7.18

(m, 1H), 6.45 (dd, *J* = 15.2, 7.0 Hz, 1H), 1.51 (s, 18H), 1.35 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz): δ 175.5 (d, $^1J_{C\text{-}P}$ = 30.7 Hz, P=*C*), 154.1, 149.9, 139.3 (d, $^1J_{C\text{-}P}$ = 52.9 Hz, *ipso*-Ar*C*), 137.4 (d, $J_{C\text{-}P}$ = 6.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 41.0 Hz), 131.0 (d, $J_{C\text{-}P}$ = 24.9 Hz), 128.8 (d, $J_{C\text{-}P}$ = 2.4 Hz), 127.8 (d, $J_{C\text{-}P}$ = 4.2 Hz), 126.7 (d, $J_{C\text{-}P}$ = 4.6 Hz), 121.8, 38.4, 35.1, 33.9 (d, $J_{C\text{-}P}$ = 6.8 Hz), 31.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.8 MHz): δ 269.2 (s).

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