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Scope and Limitations of the Base-Catalyzed Phospha-Peterson P═C Bond-Forming Reaction

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Phosphaalkenes (MesP═CRR′: R = R′ = Ph (**1a**); R = R′ = 4-FC_6H_4 (**1b**); R = Ph, R′ = 4-FC_6H_4 (**1c**); R = R′ = 4-$OMeC_6H_4$ (**1d**); R = Ph, R′ = 4-$OMeC_6H_4$ (**1e**); R = Ph, R′ = 2-pyridyl (**1f**)) are prepared from the reaction of $MesP(SiMe_3)_2$ and O═CRR′ in the presence of a trace of KOH or NaOH. The base-catalyzed phospha-Peterson reaction is quantitated by NMR spectroscopy, and isolated yields of phosphaalkene between 40 and 70% are obtained after vacuum distillation and/or recrystallization. The asymmetrically substituted phosphaalkenes (**1c**, **1e**, **1f**) form as 1:1 mixtures of *E* and *Z* isomers; however, X-ray crystallography reveals that the *E* isomers crystallize preferentially. Interestingly, *E*-**1e** and *E*-**1f** readily isomerize in solution in the dark, although the rate of isomerization is much faster when samples are exposed to light. X-ray crystal structures of **1b**, *E*-**1e**, and *E*-**1f** reveal that the P═C bond lengths (average of 1.70 Å) are in the long end of the range typically found in phosphaalkenes (1.61–1.71 Å). Attempts to prepare isolable P-adamantyl phosphaalkenes following this route were unsuccessful. Although $AdP═CPh_2$ (**2a**) is detected by ^{31}P NMR spectroscopy, attempts to isolate this species afforded the 1,2-diphosphetane $(AdPCPh_2)_2$ (**3a**), which was characterized by X-ray crystallography.

Introduction

Phosphaalkenes are attractive functional compounds that possess a (2p−3p)π bond between phosphorus and carbon.[1] Over the past thirty years, P═C bonds have evolved from exotic laboratory curiosities to encompass a rapidly growing field in which potential applications are now being envisaged. For instance, compounds with P═C bonds have recently been used in the development of new functional polymers[2−6] and have attracted attention as ligands for metal-catalyzed organic reactions.[7,8]

We have recently discovered that the P═C bonds in phosphaalkenes, by analogy with the C═C bonds of olefins, can be polymerized to afford a new phosphorus-containing polymer, poly(methylenephosphine) (eq I).[3] Phosphaalkene−styrene copolymers have also been prepared from the copolymerization of P═C and C═C bonds, and these copolymers are effective supports for the Pd-catalyzed Suzuki coupling of arylbromides and arylboronic acids.[4] Convenient preparative methods for isolable phosphaalkenes bearing a variety of substituents are needed for exploring the generality

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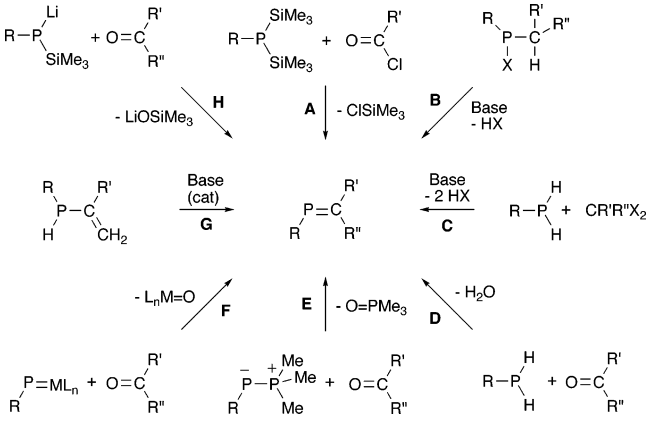
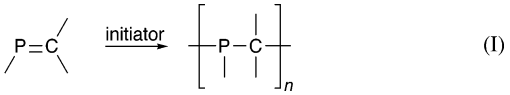
Scheme 1. Examples of Synthetic Methods Developed for the Preparation of Acyclic Phosphaalkenes



of this new polymerization reaction, improving catalyst efficiency, and exploring structure−property relations in this new class of polymer.



(I)

Several important methods for preparing isolable acyclic phosphaalkenes are shown in Scheme 1. A considerable amount of research has led to the development of the following general synthetic routes to compounds with P═C bonds: the Becker condensation followed by 1,3-silatropic rearrangement (**A**),[9] base- or thermally induced 1,2-elimination (**B**),[10,11] condensation followed by elimination (**C**[12] and **D**[13]), phospha-Wittig reactions (**E**),[14] R−P transfer from metal−phosphinidenes (**F**),[15,16] and double-bond migration reactions (**G**).[17,18]

We are particularly interested in the reaction of α-silyl phosphides with ketones or aldehydes as a route to phosphaalkene monomers for polymerization studies (**H**). This so-called phospha-Peterson reaction is an analogue of the Peterson olefination reaction,[19] and has been used extensively to prepare isolable phosphaalkenes bearing a variety of bulky substituents.[8d,20−27] An alternate base-catalyzed phospha-Peterson reaction (eq II) has been reported for the preparation of MesP═CPh$_2$.[20,28] This route represents a potentially more

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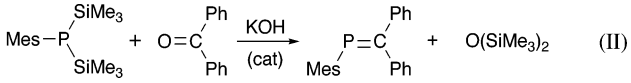
convenient method of P═C bond formation, because it is not necessary to generate $RP(Li)SiMe_3$ in situ and the sole byproduct (hexamethyldisiloxane) is volatile and easy to remove. Besides $MesP{=}CPh_2$, only a few other phosphaalkenes have been prepared by this method.



(II)

Herein, we report our studies of the scope of the base-catalyzed phospha-Peterson reaction for the synthesis of phosphaalkenes bearing P-mesityl and P-adamantyl substituents.

Experimental Section

General Procedures. All manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. Hexanes and dichloromethane were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. THF was freshly distilled from sodium/benzophenone ketyl. Distilled water was degassed prior to use. $CDCl_3$ (CIL) and acetonitrile were distilled from P_2O_5 and degassed. Benzophenone (Aldrich) was sublimed prior to use. KOH and NaOH were made anhydrous by following a literature procedure (recrystallization from EtOH and subsequent heating in vacuo).[29] 4,4′-Difluorobenzophenone, 4-fluorobenzophenone, 4,4′-dimethoxybenzophenone, 4-methoxybenzophenone, 2-benzoylpyridine, and mesitaldehyde were purchased from Aldrich and used as received. $MesP(SiMe_3)_2$,[20] $AdPH_2$,[30] and $OC(^tBu)_2$[31] were prepared following literature procedures.

Equipment. ^1H, ^{31}P, ^{19}F, and $^{13}C\{^1H\}$ NMR spectra were recorded at room temperature on Bruker Avance 300 or 400 MHz spectrometers. Chemical shifts are reported relative to residual $CHCl_3$ ($\delta = 7.24$ for ^1H), 85% H_3PO_4 as an external standard ($\delta = 0.0$ for ^{31}P), $CFCl_3$ in $CDCl_3$ as an external standard ($\delta = 0.0$ for ^{19}F), and $CDCl_3$ ($\delta = 77.0$ for ^{13}C). Assignments of NMR spectra were made with the aid of $^1H-^1H$ COSY, $^1H-^{13}C$ HMQC, and $^1H-^{13}C$ HMBC experiments. The *E* and *Z* isomers of **1** were assigned with the aid of previously published spectral data and X-ray crystal structure data obtained in this work.[21,32,33] Elemental analyses were performed in the University of British Columbia Chemistry Microanalysis Facility. Mass spectra were recorded on a Kratos MS 50 instrument in EI mode (70 eV). Samples of *E*-**1e** were irradiated using a 450 W medium-pressure mercury lamp equipped with a Pyrex filter (Corning #7740, transmits >290 nm).

$MesP{=}CPh_2$ (1a). To a stirred solution of $MesP(SiMe_3)_2$ (20.0 g, 0.067 mol) and benzophenone (12.3 g, 0.067 mol) in THF (300 mL) was added a suspension of finely ground anhydrous KOH (0.38 g, 6.8 mmol) in THF (40 mL). The pale yellow reaction mixture was stirred for 1 h.[34] An aliquot was removed and analyzed by ^{31}P NMR spectroscopy; the observation of a single signal ($\delta = 233$) suggested that **1a** had formed quantitatively. The solvent was removed in vacuo; subsequently, product **1a** was dissolved in hexanes, the solution was filtered, and the solvent was removed in vacuo. Crude yield (yellow oil) = 18 g (85%). **1a** can be purified by vacuum distillation (bp = 150−160 °C, 0.01 mmHg) followed by recrystallization from a minimal amount of cyclohexane (3×). Yield: 12.0 g (57%). To avoid the time-consuming distillation, we can remove the KOH from **1a** by extracting a CH_2Cl_2 solution of the crude product with degassed water (3×) and drying the organic layer with $MgSO_4$, followed by recrystallization from cyclohexane (3×). Yield: 72%.

^{31}P NMR ($CDCl_3$): δ 233. ^1H NMR ($CDCl_3$): δ 7.52−6.87 (m, 10H, aryl H), 6.70 (s, 2H, Mes H), 2.27 (s, 6H, *o*-CH_3), 2.20 (s, 3H, *p*-CH_3). Anal. Calcd for $C_{22}H_{21}P$: C, 83.52; H, 6.69. Found: C, 83.42; H, 6.74.

$MesP{=}C(4\text{-}FC_6H_4)_2$ (1b). $MesP(SiMe_3)_2$ (13.1 g, 0.044 mol), 4,4′-difluorobenzophenone (8.5 g, 0.039 mol), and finely ground anhydrous KOH (4 mg, 0.07 mmol) were mixed and then dissolved in THF (150 mL). The mixture was stirred, and the reaction progress was monitored by ^{31}P NMR spectroscopy. After 1 day, compound **1b** was formed quantitatively ($\delta = 234$), and the solvent was removed in vacuo. The solid residue was dissolved in hexanes (100 mL) and filtered; the solvent was removed in vacuo, leaving a yellow oil. The crude product was purified by vacuum distillation (bp = 120−140 °C; 0.01 mmHg). Yellow crystals suitable for X-ray diffraction were obtained from slow evaporation of a hexanes solution. Yield: 6.2 g (45%).

^{31}P NMR ($CDCl_3$): δ 234.3. ^{19}F NMR ($CDCl_3$): δ −112.8, −113.3. ^1H NMR ($CDCl_3$): δ 7.48 (m, 2H, *o-cis*-Ar), 7.01 (dd, $^3J_{HH} = 8$ Hz, $^3J_{FH} = 8$ Hz, 2H, *m-cis*-Ar), 6.82 (m, 2H, *o-trans*-Ar), 6.74 (dd, $^3J_{HH} = 9$ Hz, $^3J_{FH} = 9$ Hz, 2H, *m-trans*-Ar), 6.72 (s, 2H, *m*-Mes), 2.25 (s, 6H, *o*-CH_3), 2.21 (s, 3H, *p*-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 190.7 (d, $^1J_{PC} = 44$ Hz, P═*C*), 163.6 (dd, $^5J_{PC} = 5$ Hz, $^1J_{FC} = 249$ Hz, *p-cis*-Ar), 162.0 (d, $^1J_{FC} = 248$ Hz, *p-trans*-Ar), 140.8 (d, $^2J_{PC} = 25$ Hz, *i-cis*-Ar), 140.2 (d, $^2J_{PC} = 7$ Hz, *o*-Mes), 139.1 (d, $^2J_{PC} = 15$ Hz, *i-trans*-Ar), 138.7 (s, *p*-Mes), 135.9 (d, $^1J_{PC} = 43$ Hz, *i*-Mes), 130.4 (dd, $^3J_{PC} = 7$ Hz, $^3J_{FC} = 7$ Hz, *o-trans*-Ar), 129.3 (dd, $^3J_{PC} = 19$ Hz, $^3J_{FC} = 8$ Hz, o-*cis*-Ar), 128.4 (s, *m*-Mes), 115.2 (d, $^2J_{FC} = 22$ Hz, *m-cis*-Ar), 114.5 (d, $^2J_{FC} = 22$ Hz, *m-trans*-Ar), 22.1 (d, $^3J_{PC} = 9$ Hz, *o*-*C*H_3), 21.0 (s, *p*-*C*H_3). MS (EI, 70 eV): 353, 352 [24, 100; M^+]; 351 [43; $M^+ - H$]; 258, 257 [4, 20; $M^+ - 4\text{-}FC_6H_4$]; 256 [26, $M^+ - 4\text{-}FC_6H_4 + H$]; 203 [46; $M^+ - MesP + H$]. Anal. Calcd for $C_{22}H_{19}F_2P$: C, 74.99; H, 5.44. Found: C, 74.77; H, 5.36.

$MesP{=}C(Ph)(4\text{-}FC_6H_4)$ (1c). $MesP(SiMe_3)_2$ (12.7 g, 0.043 mol), 4-fluorobenzophenone (8.6 g, 0.043 mol), and anhydrous KOH (6 mg, 0.1 mmol) were mixed as solids and then dissolved in THF (80 mL). The mixture was stirred, and the reaction progress was monitored by ^{31}P NMR spectroscopy. After 4 days, compound **1c** was formed quantitatively ($\delta = 234$, 233), and the solvent was removed in vacuo. The solid residue was dissolved in hexanes (50 mL) and filtered; the solvent was removed in vacuo, leaving a dark red oil. The crude product was purified by vacuum distillation (170−180 °C, 0.01 mmHg). The product is a viscous yellow oil that does not solidify on standing. Yield: 8.3 g (58%).

^{31}P NMR ($CDCl_3$): δ 234.0 (*Z*), 232.6 (*E*). ^{19}F NMR ($CDCl_3$) (*E*/*Z* mixture): δ −113.8, −114.6. ^1H NMR ($CDCl_3$) (*E*/*Z* mixture): δ 7.5−6.7 (m, 11H, Ar), 2.23 (s, 6H *o*-CH_3), 2.20, 2.18 (s, 3H, *p*-CH_3). MS (EI, 70 eV): 336, 335, 334 [3, 22, 100; M^+]; 333 [51; $M^+ - H$]; 186, 185 [9, 45; $M^+ - MesP + H$]. Anal. Calcd for $C_{22}H_{20}FP$: C, 79.03; H, 6.03. Found: C, 78.79; H, 5.87.

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(34) The reaction time is highly variable and may require a few days for completion, depending on scale, reagent concentration, and amount of KOH or NaOH added. We have found that careful monitoring by ^{31}P NMR is required. In the case of a sluggish reaction, additional KOH or NaOH may be needed.

MesP=C(4-OMeC$_6$H$_4$)$_2$ (1d). MesP(SiMe$_3$)$_2$ (13.0 g, 0.044 mol), 4,4′-dimethoxybenzophenone (10.6 g, 0.044 mol), and anhydrous KOH (0.10 g, 1.7 mmol) were mixed as solids and then dissolved in THF (150 mL). The reaction mixture was stirred, and the reaction progress was monitored by ^{31}P NMR spectroscopy. After 2 days, compound **1d** was formed quantitatively (δ = 217), and the solvent was removed in vacuo. The solid residue was extracted with hexanes (3 × 50 mL) and filtered; the solvent was removed in vacuo, leaving a yellow solid. The crude product was purified by recrystallization from a mixture of hexanes and THF at −70 °C. Yield: 8.0 g (49%).

^{31}P NMR (CDCl$_3$): δ 217.3. ^{1}H NMR (CDCl$_3$): δ 7.61 (d, $^3J_{HH}$ = 7 Hz, 2H, *o-cis*-Ar), 6.97 (d, $^3J_{HH}$ = 7 Hz, 2H, *m-cis*-Ar), 6.94 (d, $^3J_{HH}$ = 8 Hz, 2H, *o-trans*-Ar), 6.83 (s, 2H, *m*-Mes), 6.68 (d, $^3J_{HH}$ = 9 Hz, 2H, *m-trans*-Ar), 3.87 (s, 3H, *Z*-OC*H*$_3$), 3.73 (s, 3H, *E*-OC*H*$_3$), 2.40 (s, 6H, *o*-C*H*$_3$), 2.30 (s, 3H, *p*-C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 192.1 (d, $^1J_{PC}$ = 44 Hz, P=*C*), 160.4 (d, $^5J_{PC}$ = 4 Hz, *p-cis*-Ar), 158.8 (s, *p-trans*-Ar), 140.2 (d, $^2J_{PC}$ = 7 Hz, *o*-Mes), 137.7 (d, $^2J_{PC}$ = 25 Hz, *i-cis*-Ar), 137.8 (s, *p*-Mes), 136.7 (d, $^1J_{PC}$ = 43 Hz, *i*-Mes), 136.0 (d, $^2J_{PC}$ = 15 Hz, *i-trans*-Ar), 130.1 (d, $^3J_{PC}$ = 6 Hz, *o-trans*-Ar), 129.0 (d, $^3J_{PC}$ = 19 Hz, *o*-cis-Ar), 128.1 (s, *m*-Mes), 113.4 (s, *m-cis*-Ar), 112.6 (s, *m-trans*-Ar), 55.0 (s, *Z*-OCH$_3$), 54.7 (s, *E*-OCH$_3$), 22.1 (d, $^3J_{PC}$ = 9 Hz, *o*-*C*H$_3$), 20.9 (s, *p*-*C*H$_3$). MS (EI, 70 eV): 378, 377, 376 [4, 27, 100; M$^+$]; 375 [30; M$^+$ − H]; 362, 361 [4, 17; M$^+$ − CH$_3$]; 270, 269, 268 [4, 28, 93; M$^+$ − 4-C$_6$H$_4$OCH$_3$ − H]; 228, 227 [6, 28; M$^+$ − MesP + H]. Anal. Calcd for C$_{24}$H$_{25}$O$_2$P: C, 76.58; H, 6.69. Found: C, 76.30; H, 6.71.

MesP=C(Ph)(4-OMeC$_6$H$_4$) (1e). MesP(SiMe$_3$)$_2$ (4.05 g, 0.014 mol), 4-methoxybenzophenone (2.90 g, 0.014 mol), and anhydrous KOH (4 mg, 0.07 mmol) were mixed as solids. The solids were dissolved in THF (50 mL) and stirred for 1 day. Analysis of an aliquot removed from the reaction mixture by ^{31}P NMR spectroscopy showed the quantitative formation of phosphaalkenes (δ = 226, 224). After solvent removal, the solid residue was extracted in hexanes (3 × 20 mL) and filtered; the solvent was removed in vacuo, revealing a yellow liquid. The crude product was purified by distillation at 189 °C (0.01 mmHg). Yellow crystals suitable for X-ray diffraction were obtained from slow evaporation of a hexanes solution. Yield: 2.05 g (42%).

^{31}P NMR (CDCl$_3$): δ 225.6 (*Z*), 223.7 (*E*). ^{1}H NMR (CDCl$_3$) (*E* isomer): δ 7.48 (dd, $^3J_{HH}$ = 9 Hz, $^4J_{PH}$ = 3 Hz, 2H, *o-trans*-Ph), 7.11−7.01 (m, 3H, *m,p-cis*-Ph), 6.87 (d, $^3J_{HH}$ = 7 Hz, 2H, *o-cis*-Ph), 6.84 (d, $^3J_{HH}$ = 9 Hz, 2H, *m-trans*-Ph), 6.68 (s, 2H, *m*-Mes), 3.82 (s, 3H, −OC*H*$_3$), 2.26 (s, 6H, *o*-C*H*$_3$), 2.18 (s, 3H, *p*-C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$) (*E*-isomer): 192.9 (d, $^1J_{PC}$ = 44 Hz, P=*C*), 160.6 (d, $^5J_{PC}$ = 4 Hz, *p*-Ar), 143.3 (d, $^2J_{PC}$ = 14 Hz, *i*-Ar), 140.4 (d, $^2J_{PC}$ = 7 Hz, *o*-Mes), 138.2 (s, *p*-Mes), 137.7 (d, $^2J_{PC}$ = 25 Hz, *i*-Ph), 136.4 (d, $^1J_{PC}$ = 43 Hz, *i*-Mes), 128.9 (d, $^3J_{PC}$ = 20 Hz, *o*-Ph), 128.6 (d, $^3J_{PC}$ = 7 Hz, *o*-Ar), 128.1 (s, *m*-Mes), 127.3 (s, *m,p*-Ph), 113.6 (s, *m*-Ar), 55.4 (s, −OCH$_3$), 22.3 (d, $^3J_{PC}$ = 9 Hz, *o*-*C*H$_3$), 21.0 (s, *p*-*C*H$_3$). MS (EI, 70 eV): 348, 347, 346 [3, 24, 100; M$^+$]; 345 [27; M$^+$ − H]; 331 [7; M$^+$ − CH$_3$]; 269 [6; M$^+$ − Ph]; 240, 239, 238 [4, 16, 72; M$^+$ − 4-MeOC$_6$H$_4$ − H]; 198, 197 [6, 30; M$^+$ − MesP + H]. Anal. Calcd for C$_{23}$H$_{23}$OP: C, 79.75; H, 6.69. Found: C, 80.15; H, 6.35.

MesP=C(Ph)(2-py) (1f). MesP(SiMe$_3$)$_2$ (16.2 g, 0.055 mol), 2-benzoylpyridine (10.0 g, 0.055 mol), and anhydrous NaOH (10 mg, 0.25 mmol) were mixed. The solids were dissolved in THF (100 mL) and stirred for 3 days. ^{31}P NMR spectroscopy analysis of an aliquot removed from the reaction mixture showed the quantitative formation of phosphaalkenes (δ = 260, 242). After solvent removal, the solid residue was extracted into hexanes (50 mL) and filtered; the solvent was removed in vacuo, revealing a yellow-green solid. The crude product was purified by slow evaporation of an acetonitrile:hexanes (3:1) mixture to afford yellow crystals. Yield: 8.3 g (48%).

^{31}P NMR (CDCl$_3$): δ 260.1 (*E*), 242.1 (*Z*). ^{1}H NMR (CDCl$_3$) (*E/Z* mixture): δ 8.67 (d, $^3J_{HH}$ = 4 Hz, 1H, *E-o*-py), 8.46 (d, $^3J_{HH}$ = 4 Hz, 1H, *Z-o*-py), 7.6−6.7 (br m, 16H, *E/Z*-Ar), 6.68, 6.67 (s, 4H, *E,Z-m*-Mes), 2.28, 2.26 (s, 12H, *Z,E-o*-C*H*$_3$), 2.17, 2.16 (s, 6H, *E,Z-p*-C*H*$_3$). MS (EI, 70 eV): 319, 318, 317 [3, 24, 100; M$^+$]; 316 [9; M$^+$ − H]; 303, 302 [3, 11; M$^+$ − CH$_3$]; 241, 240 [7, 40; M$^+$ − Ph]; 239 [14; M$^+$ − C$_6$H$_6$]; 226 [34; M$^+$ − py − H]; 169, 168, 167 [32, 97; M$^+$ − MesP + H]; 167 [32; M$^+$ − MesP]; 149 [33; MesP$^+$ + H]. Anal. Calcd for C$_{21}$H$_{20}$NP: C, 79.47; H, 6.35; N, 4.41. Found: C, 79.38; H, 6.35; N, 4.36.

AdP(SiMe$_3$)$_2$. To a solution of AdPH$_2$ (3.45 g, 20.5 mmol) in THF (40 mL) was added MeLi (58 mL, 1.4 M, 81 mmol) at −78 °C. The reaction mixture was slowly warmed to room temperature, whereupon it was stirred for a further 30 min. The resulting dark orange solution was cooled to −78 °C; Me$_3$SiCl (11 mL) was added, and the reaction mixture was again warmed to room temperature. An aliquot was taken for ^{31}P NMR spectroscopy analysis (AdP(SiMe$_3$)$_2$: δ = −106 (s)). Often, after the first silylation step, we observed a mixture of AdP(SiMe$_3$)$_2$, AdP(H)SiMe$_3$, and AdPH$_2$. In this instance, the solvent/Me$_3$SiCl was removed in vacuo, and the resulting mixture was redissolved in freshly distilled THF, relithiated, and silylated following the above procedure. Typically, after one relithiation, AdP(SiMe$_3$)$_2$ was formed quantitatively (according to ^{31}P NMR). The solvent was then removed in vacuo. The yellow solid residue was extracted with hexanes (3 × 50 mL) and filtered, and the solvent was removed. The crude product (a colorless liquid) was purified by distillation (bp = 110 °C, 5 mmHg). Yield: 4.68 g (73%).

^{31}P NMR (C$_6$D$_6$): δ −106 (s). ^{1}H NMR (C$_6$D$_6$): δ 2.04 (m, 6H, 2-Ad), 1.83 (s, 3H, 3-Ad), 1.62 (s, 6H, 4-Ad), 0.35 (d, $^3J_{PH}$ = 4 Hz, 18H, C*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 46.4 (d, $^2J_{PC}$ = 8 Hz, 2-Ad), 36.8 (s, 4-Ad), 35.2 (d, $^1J_{PC}$ = 14 Hz, 1-Ad), 29.9 (d, $^3J_{PC}$ = 8 Hz, 3-Ad), 3.89 (d, $^2J_{PC}$ = 12 Hz, *C*H$_3$).

AdP(H)SiMe$_3$. To a solution of AdPH$_2$ (1.16 g, 6.9 mmol) in Et$_2$O (20 mL) was added MeLi (7 mL, 1.5 M, 10.5 mmol) at −78 °C. The reaction mixture was slowly warmed to room temperature, whereupon it was stirred for a further 45 min. The resulting yellow suspension was cooled to −78 °C, Me$_3$SiCl (1.5 mL) was added, and the reaction mixture was again warmed to room temperature for 30 min. An aliquot was taken for ^{31}P NMR spectroscopy analysis (AdP(H)SiMe$_3$: δ = −84.7 (d)). The solvent was then removed in vacuo. The yellow solid residue was extracted with hexanes (3 × 20 mL) and filtered, and the solvent was removed in vacuo. The crude product (a colorless liquid) was purified by distillation (bp = 80 °C, 5 mmHg). Yield: 1.19 g (72%).

^{31}P NMR (C$_6$D$_6$): δ −84.7 (d, $^1J_{PH}$ = 194 Hz). ^{1}H NMR (C$_6$D$_6$): δ 2.32 (d, $^1J_{PH}$ = 194 Hz, 1H, P*H*), 1.88 (m, 6H, 2-Ad), 1.80 (s, 3H, 3-Ad), 1.59 (s, 6H, 4-Ad), 0.25 (d, $^3J_{PH}$ = 4 Hz, 9H, C*H*$_3$).

In situ Preparation of AdP(Li)SiMe$_3$. *Method A.* To a solution of AdP(SiMe$_3$)$_2$ (1.66 g, 5.3 mmol) in THF (25 mL) was added MeLi (7.1 mL, 1.4 M, 9.9 mmol). The reaction mixture was heated to reflux overnight. The quantitative formation of AdP(Li)SiMe$_3$ was confirmed by ^{31}P NMR [δ = −96.9 (s)]. *Method B.* To a solution of AdP(H)SiMe$_3$ (1.2 g, 5.0 mmol) in THF (20 mL) was added MeLi (1.5 M, 4.0 mL, 6.0 mmol) at −78 °C. The reaction mixture was warmed to room temperature, and the quantitative formation of AdP(Li)SiMe$_3$ was established by ^{31}P NMR (δ = −96.9 (s)).

Table 1. X-ray Crystallographic Data for **1b**, *E*-**1E**, *E*-**1f**, and **3A**+THF

	1b	*E*-**1e**	*E*-**1f**	**3a**+THF
formula	$C_{22}H_{19}PF_2$	$C_{23}H_{23}OP$	$C_{21}H_{20}NP$	$C_{50}H_{58}P_2O$
fw	352.36	346.38	317.35	736.96
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$C2/c$
color	yellow	yellow	yellow	clear
a (Å)	9.3394(2)	12.5689(8)	11.016(1)	22.447(2)
b (Å)	14.1908(3)	10.4921(6)	17.254(2)	15.2803(9)
c (Å)	15.6207(3)	15.6160(10)	9.475(1)	13.533(1)
α (deg)	69.626(8)	90.0	90.0	90.0
β (deg)	71.699(8)	109.345(3)	107.89(1)	122.037(3)
γ (deg)	86.12(1)	90.0	90.0	90.0
V (Å^3)	1840.6(1)	1943.1(2)	1713.8(3)	3934.8(5)
T (K)	173.0	173.0	173.0	173.0
Z	4	4	4	4
μ(Mo Kα) (cm^{-1})	1.69	1.48	1.60	1.49
cryst size (mm^3)	0.50 × 0.25 × 0.15	0.40 × 0.40 × 0.20	0.20 × 0.20 × 0.05	0.35 × 0.30 × 0.20
calcd density (Mg m^{-3})	1.271	1.184	1.230	1.244
2θ(max) (deg)	55.7	55.7	55.6	55.7
no. of reflns	16 453	37 662	42 105	18 463
no. of unique data	7452	4594	4044	4621
R(int)	0.036	0.0309	0.061	0.053
refln/param ratio	16.52	20.33	19.08	15.32
R1[a]	0.041; $I > 3\sigma(I)$	0.0389; $I > 2\sigma(I)$	0.043; $I > 2\sigma(I)$	0.042; $I > 2\sigma(I)$
wR2 (all data)[b]	0.123	0.1204	0.124	0.112
GOF	1.07	1.091	1.05	1.00

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2\ [\text{all data}]) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

(AdPCPh)$_2$ (3a). To a solution of AdP(Li)SiMe$_3$ (4.9 mmol) was added dropwise a solution of O═CPh$_2$ (1.08 g, 5.9 mmol) in THF (10 mL). An aliquot of the dark orange reaction mixture was removed and analyzed by ^{31}P NMR spectroscopy. A singlet resonance was observed at 286 ppm, suggesting quantitative formation of a phosphaalkene; however, over a few hours, a second signal at 28 ppm was detected in addition to the signal assigned to phosphaalkene. The reaction mixture was quenched with Me$_3$SiCl (0.76 mL, 6.0 mmol). Over a period of ca. 2 days, the ^{31}P NMR spectrum of the reaction mixture showed only one signal at 28 ppm. After solvent removal, the solid residue was extracted with hexanes (3 × 20 mL) and filtered; the solvent was removed in vacuo, affording a yellow oil. Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of a THF solution. Yield: 0.71 g (43%).

^{31}P NMR ($CDCl_3$): δ 28 (s). ^{1}H NMR ($CDCl_3$): δ 8.17 (d, $^3J_{HH}$ = 8 Hz, 4H, *o*-Ph), 7.48 (t, $^3J_{HH}$ = 7 Hz, 4H, *m*-Ph), 7.11 (t, $^3J_{HH}$ = 7 Hz, 4H, *m*-Ph), 6.82 (m, 4H, *p*-Ph), 6.54 (d, 4H, *o*-Ph), 1.8−1.4 (m, 30H, Ad). MS (70 eV, EI): 665, 664 [0.10, 0.17; M$^+$]; 333, 332 [3, 12; AdPCPh$_2^+$], 168, 167 [10, 50; (AdPH)$^+$ or (HCPh$_2$)$^+$], 136, 135 [14, 100; Ad$^+$].

Attempted Preparation of AdP═CR′R" (2b−d). To a cooled (−78 °C) solution of AdP(Li)SiMe$_3$ (ca. 1 mmol) in THF (5 mL) was added dropwise a solution of ketone/aldehyde (1 equiv) in THF. An aliquot was immediately removed from the reaction mixture and analyzed using ^{31}P NMR spectroscopy. The NMR spectroscopic data are summarized in Table 3. None of these phosphaalkenes were isolable.

X-ray Crystallography. All single crystals were immersed in oil and mounted on a glass fiber. Data were collected on a Rigaku/ADSC CCD diffractometer (**1b** and **3a**) or a Bruker X8 APEX diffractometer (*E*-**1e** and *E*-**1f**) with graphite-monochromated Mo Kα radiation. All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms. All data sets were corrected for Lorentz and polarization effects. All calculations on crystal **1b** and **3a** were performed using the teXsan[35] crystallographic software package from the Molecular Structure Corporation, whereas all refinements of *E*-**1e** and *E*-**1f** were performed using the SHELXTL[36] crystallographic software package from Bruker-AXS.

Compound *E*-**1f** is disordered by a 180° rotation about the C1−C2 bond. The disorder was modeled by placing partial nitrogen and carbon in both positions ortho to C2 (using SHELXL EXYZ and EADP functions) and refining their respective populations (occupancy 0.84(1) and 0.16(1)). Compound **3a** crystallizes with a half-molecule of THF (on a C_2 axis), and the adamantyl group was disordered. The disorder was modeled in two orientations, with relative populations of 0.86 and 0.14 for the major and minor fragments, respectively. Additional crystal data and details of the data collection and structure refinement are given in Table 1. Further details are included in the Supporting Information.

Results and Discussion

The base-catalyzed phospha-Peterson reaction can be used to prepare P-mesityl phosphaalkenes bearing several C-aryl substituents. By slightly modifying Becker's original procedure for **1a**,[20] we have prepared several isolable P-mesityl phosphaalkenes (**1b**−**f**) from MesP(SiMe$_3$)$_2$ and the appropriate ketone in the presence of a catalytic quantity of anhydrous KOH or NaOH.[37] After vacuum distillation and/or recrystallization, the isolated yields of analytically pure phosphaalkene were between 43 and 72%, and each could be prepared on multigram scales. Interestingly, we have found that compounds **1a**−**e** are amenable to aqueous workup provided they are kept free from oxygen. Aqueous workup allows for easy removal of KOH (or KOSiMe$_3$) and obviates the need for distillation. Unlike the other phos-

(35) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1985 and 1992.
(36) *SHELXTL version 5.1*; Bruker AXS Inc.: Madision, WI, 1997.
(37) A ^{31}P NMR study has mentioned phosphaalkenes **1c**−**e**, and their chemical shifts have been reported. These compounds were prepared in situ using the phospha-Peterson route (Scheme 1, path H); however, no experimental details were provided, and the compounds were not isolated. See ref 21.

Table 2. Important Metrical Parameters for Phosphaalkenes Bearing P-Mes and C−Ar Substituents

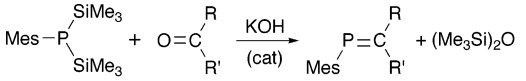
	1a	**1a**	**1b**[a]	**1d**[a]	*E*-**1e**	*E*-**1f**	*Z*-MesP═C(4-BrC_6H_4)(4-MeOC_6H_4)	*E*-MesP═C(2-^{i}PrC_6H_4)Ph
				Bond Lengths				
P═C	1.692(3)	1.693(2)	1.688(2) 1.691(2)	1.698(3) 1.696(3)	1.7082(13)	1.7043(16)	1.692(5)	1.682(2)
P−C_{Mes}	1.828(3)	1.830(2)	1.831(2) 1.830(2)	1.821(3) 1.820(3)	1.8418(13)	1.8378(16)	1.827(5)	1.835(2)
C−C_{trans}	1.491(5)	1.493(5)	1.486(2) 1.491(2)	1.481(3) 1.484(4)	1.4884(17)	1.496(2)	1.482(7)	1.500(2)
C−C_{cis}	1.487(4)	1.489(2)	1.484(2) 1.482(2)	1.479(4) 1.486(4)	1.4908(17)	1.498(2)	1.491(7)	1.482(2)
				Bond Angles				
∠C_{Mes}−P═C	107.5(2)	107.6(2)	107.14(9) 108.17(8)	108.8(13) 108.8(13)	106.51(6)	107.80(7)	105.8(2)	106.20(8)
∠P═C−C_{trans}	116.2(2)	118.0(2)	117.8(1) 114.9(1)	115.11(19) 114.9(2)	115.66(9)	116.87(11)	115.9(3)	116.4(1)
∠P═C−C_{cis}	127.2(2)	124.8(2)	126.5(1) 128.3(1)	128.01(19) 127.6(2)	126.51(9)	125.41(11)	127.0(4)	128.5(1)
∠C_{cis}−C−C_{trans}	116.6(2)	117.1(3)	115.7(2) 116.8(1)	116.8(2) 117.5(2)	117.72(10)	117.48(13)	117.1(4)	115.1(1)
				Angles between Planes[b]				
Mes	71	72.2	71.8 70.1	64.5 68.9	71.9	70.4	70.4	69.5
Ar_{trans}	36.6	21.4	45.1 32.9	45.8 41.4	33.7	22.4	37.4	66.6
Ar_{cis}	42.9	59.2	54.8 56.0	37.1 37.1	49.0	57.6	46.5	47.9
reference	11h	40	this work	42	this work	this work	42	41

[a] Two independent molecules are present in the asymmetric unit. Data on the top line are for molecule 1; the bottom line, for molecule 2. [b] The angle between the mean plane of the specified aryl ring atoms to the mean plane C_{ipso}−P═C−(C_{trans})(C_{cis}) atoms.

Table 3. Synthesis and the ^{31}P NMR Chemical Shifts of Phosphaalkenes 1 and 2, RP═CR′R″

compd	R	R′	R″	^{31}P NMR (ppm)
1a	Mes	Ph	Ph	233
1b	Mes	4-FC_6H_4	4-FC_6H_4	234
1c	Mes	Ph	4-FC_6H_4	234 (*Z*), 233 (*E*)
1d	Mes	4-OMeC_6H_4	4-OMeC_6H_4	217
1e	Mes	Ph	4-OMeC_6H_4	226 (*Z*), 224(*E*)
1f	Mes	Ph	2-py	260 (*E*), 242 (*Z*)
2a	Ad	Ph	Ph	286
2b	Ad	Me	Me	257
2c	Ad	Mes	H	299, 293
2d	Ad	^{t}Bu	^{t}Bu	not formed

phaalkenes, 2-pyridyl-substituted phosphaalkene (**1f**) is very sensitive to moisture and must be recrystallized from a mixture of acetonitrile and hexanes. Compound **1f** is a rare example of a 2-pyridyl-substituted phosphaalkene and is of interest as a bidentate chelating ligand for transition metals. Previously reported pyridyl-substituted phosphaalkenes have employed the bulkier supermesityl substituent at phosphorus (e.g., Mes*P═CH(2-py),[22] Mes*P═CH(2,6-py)HC═PMes*,[22] and Mes*P═C(R)(2-py),[26,38] with R = H, $SiMe_3$, and ^{t}Bu; and Mes* = 2,4,6-tri-*tert*-butylphenyl).



1a: R=R'=Ph
1b: R=R'=4-FC_6H_4
1c: R=Ph, R'=4-FC_6H_4
1d: R=R'=4-OMeC_6H_4
1e: R=Ph, R'=4-OMeC_6H_4
1f: R=Ph, R'=2-pyridyl

The presence of two signals of equal intensity in ^{31}P NMR spectra of the phosphaalkene reaction mixtures suggests that the compounds **1c**, **1e**, and **1f** form as mixtures of *E* and *Z* isomers in approximately 1:1 ratios. X-ray structure determinations (discussed below) for single crystals of **1e** and **1f** reveal that each mixture crystallizes as the *E* isomer. Interestingly, the ^{31}P NMR spectra of these crystals dissolved in $CDCl_3$, THF, or C_6H_6 show signals for both *E* and *Z* isomers; therefore, it can be concluded that a facile cis/trans isomerization is taking place in solution. The cis/trans isomerization of phosphaalkenes has been observed previously; however, it is usually photochemical and requires UV irradiation.[1m,21,33,39] In the case of *E*-**1e** and *E*-**1f**, ^{31}P NMR spectroscopic studies in C_6H_6 reveal that isomerization occurs in the absence of light (ca. 48 h to equilibrium) but is faster when solutions are exposed to sunlight (<24 h to equilibrium.). Interestingly, equilibrium is reached in just 30 min when a C_6H_6 solution of *E*-**1e** is irradiated with UV light (>290 nm, 25 °C).

A search of the Cambridge Crystallographic Database found 20 P═C compounds with P-mesityl substituents, of which several were metal complexes or (σ^3, λ^5) systems. To further investigate the structural features and bonding in uncomplexed P-mesityl phosphaalkenes, we have analyzed three representative compounds by X-ray crystallography. A summary of cell constants and data collection parameters for **1b**, *E*-**1e**, and *E*-**1f** are included in Table 1. The molecular structures of phosphaalkenes **1b**, *E*-**1e**, and *E*-**1f** are shown in Figures 1− 3, respectively. Important

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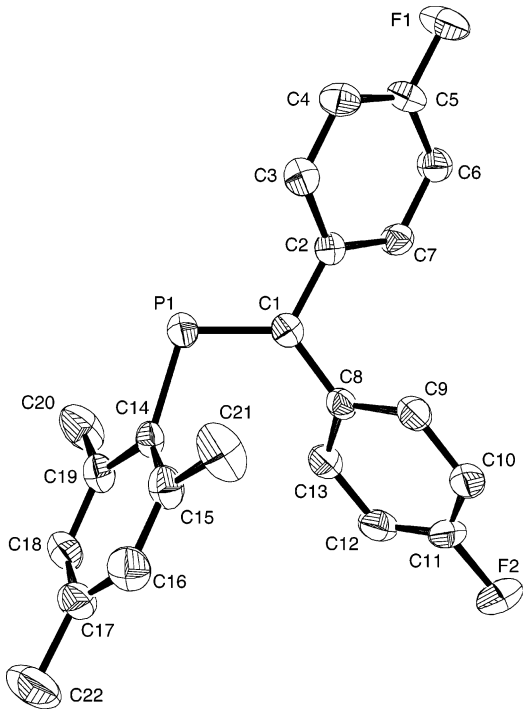

Figure 1. Molecular structure of MesP═C(4-FC_6H_4)$_2$ (**1b**). Two virtually identical molecules appear in the asymmetric unit. Metrical parameters are given for one of the two molecules. Ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.688(2), P(1)−C(14) 1.831(2), C(1)−C(2) 1.486(2), C(1)−C(8) 1.484(2), F(1)−C(5) 1.358(2), F(2)−C(11) 1.363(2); C(1)−P(1)−C(14) 107.14(9), P(1)−C(1)−C(2) 117.8(1), P(1)−C(1)−C(8) 126.5(1), C(2)−C(1)−C(8) 115.7(2).

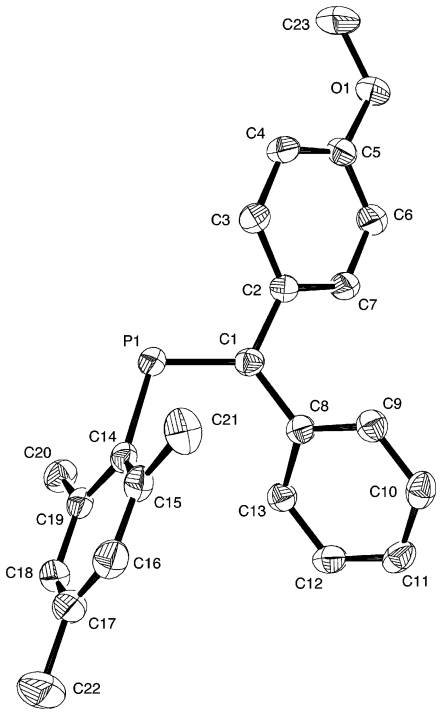

Figure 2. Molecular structure of MesP═C(Ph)(4-$OMeC_6H_4$) (*E*-**1e**). Ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.7082(13), P(1)−C(14) 1.8418(13), C(1)−C(2) 1.4884(17), C(1)−C(8) 1.4908(17); C(2)−C(1)−P(1) 115.66(9), C(8)−C(1)−P(1) 126.51(9), C(1)−P(1)−C(14) 106.51(6), C(2)−C(1)−C(8) 117.72(10), C(5)−O(1)−C(23) 117.86(13).

metricalparameters for **1b**, *E*-**1e**, and *E*-**1f** are tabulated in Table 2 and, for comparison, the metrical parameters are also provided for the closely related phosphaalkenes **1a**,[11h,40] *E*-MesP═CPh(2-^{i}PrC$_6$H$_4$),[41] MesP═C(4-BrC_6H_4)(4-$MeOC_6H_4$),[42] and **1d**.[42]

The methoxy-substituted *E*-**1e** and 2-pyridyl-substituted *E*-**1f** possess slightly longer P═C bond lengths (**1e**, 1.7082-(13) Å; **1f**, 1.7043(16) Å) than those in **1a** (1.692(3), 1.693-(2) Å) and **1b** (1.688(2), 1.691(2) Å). Overall, the P═C bonds in P-mesityl phosphaalkenes are at the long end of the range typically found for C-substituted phosphaalkenes (1.61−1.71 Å)[1h] but are shorter than the P═C bonds in inversely polarized phosphaalkenes (1.70−1.76 Å).[1c] Interestingly, the P−C_{Mes} bonds for the P-mesityl phosphaalkenes (ca. 1.83 Å) are short compared with a typical P−C single bond (range: 1.85−1.90 Å).[43] The slight elongation of the P═C bond and shortening of the P−C_{Mes} bond suggests some π-conjugation between the Mes group and the P═C bonds. However, the large angles between the Mes and P═C planes

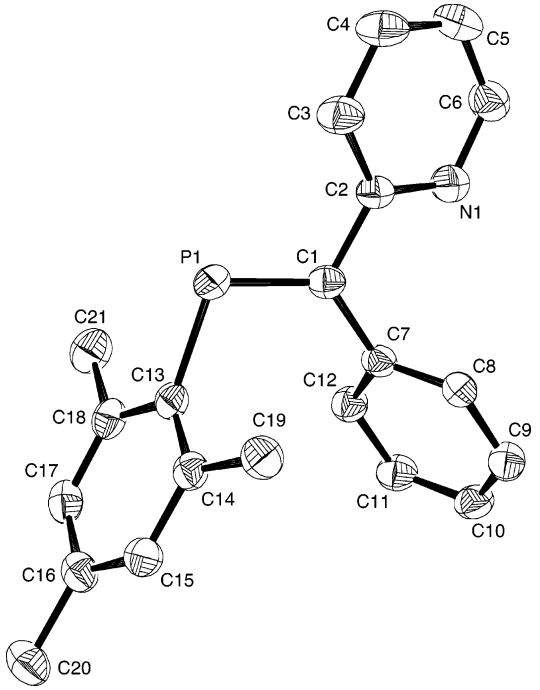

Figure 3. Molecular structure of MesP═C(Ph)(2-py) (*E*-**1f**). Ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.7043-(16), P(1)−C(13) 1.8378(16), C(1)−C(2) 1.496(2), C(1)−C(7) 1.498(2); C(2)−C(1)−P(1) 116.87(11), C(7)−C(1)−P(1) 125.41(11), C(1)−P(1)−C(13) 107.80(7), C(2)−C(1)−C(7) 117.48(13).

in each phosphaalkene (ca. 71°) are consistent with less π-conjugation between P═C and Mes than between the

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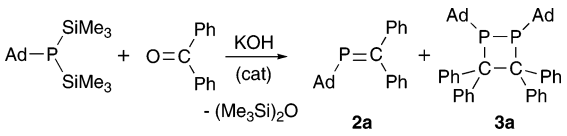
P═C and Ar_{trans} (angle between planes: 21.4−45.1°]. For comparison, the angles between the P═C bond and Ph planes in the C−H functional phosphaalkenes *E*-Mes*P═CHPh[44] and *E*,*E*-PhHC═PArP═CHPh[14c] are 14.2 and 22°, respectively. Of course, in addition to intramolecular electronic and steric effects, the metrical parameters are also influenced by intermolecular crystal packing effects. Nevertheless, the data do support the notion that there is some π-interaction between the aryl substituents and the P═C bond in P-Mes phosphaalkenes.

The bond angles at phosphorus, ∠C−P═C, in all the P-Mes phosphaalkenes are ca. 108°. This is consistent with a high degree of s-character in the lone pair on phosphorus, with the σ-bonds being higher in p-character. The geometry at C1 is essentially planar in each compound (sum of angles 360(1)° in each case). It is interesting to note that Ar_{cis} (∠P═C−C_{cis} ≈ 127°) bends further away from the P═C bond than Ar_{trans} (∠P═C−C_{trans} ≈ 116°]. This fact reflects the greater steric congestion between the Mes and Ph groups in the former.

Thus far, we have shown that the base-catalyzed phospha-Peterson reaction is a clean and simple method for phosphaalkenes bearing P-mesityl substituents and C-aryl substituents. Given our recent interest in phosphaalkene−styrene copolymers as supports for Pd-catalyzed Suzuki coupling reactions, we hypothesized that poly(methylenephosphines) bearing bulky P-alkyl substituents (i.e., Ad) might give more active catalysts.[45] It seemed logical to extend the base-catalyzed phospha-Peterson reaction to P-adamantyl phosphaalkenes. Therefore, under conditions analogous to those used to prepare **1a**−**f**, we treated AdP($SiMe_3$)$_2$ with benzophenone in the presence of a trace of KOH. The reaction was monitored by ^{31}P NMR spectroscopy, and signals were observed that could be attributed to unreacted AdP($SiMe_3$)$_2$ (δ = −106), the desired phosphaalkene (**2a**) (δ = 286), and an unknown product later determined to be **3a** (δ = 28). Despite several attempts to improve the reaction conditions or the isolation procedures, **2a** could not be generated quantitatively nor could it be separated from the other species.



Given these difficulties, we attempted to use the standard phospha-Peterson route (Scheme 1, Path **H**) to access **2a**. The complete lithiation of AdP($SiMe_3$)$_2$ requires reflux conditions in THF. It is more convenient to prepare AdP(Li)$SiMe_3$ (δ^{31}_P = −96.9) (Figure 4a) from the room-temperature reaction of AdP(H)$SiMe_3$ and MeLi (1 equiv). In contrast to the base-catalyzed reaction described above, treating the lithium phosphide with benzophenone results in the clean, near quantitative formation of **2a** (δ^{31}_P = 286) (see Figure 4b). Unfortunately, **2a** is not isolable and slowly (ca. 48 h) dimerizes to **3a** (δ = 28) according to ^{31}P NMR spectroscopy (Figure 4c).

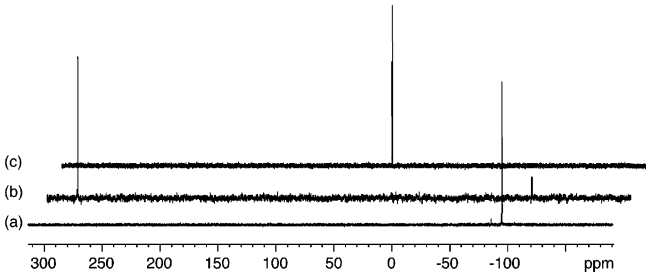


Figure 4. Reaction of AdP(Li)$SiMe_3$ and O═CPh_2 in THF. (a) ^{31}P NMR spectrum of AdP(Li)$SiMe_3$ in THF (prepared from AdP(H)$SiMe_3$ + MeLi); (b) ^{31}P NMR spectrum of **2a** (δ = 286) recorded immediately after O═CPh_2 was added to AdP(Li)$SiMe_3$; (c) ^{31}P NMR spectrum of **3a** (δ = 28) formed from **2a** after 2 days in THF.

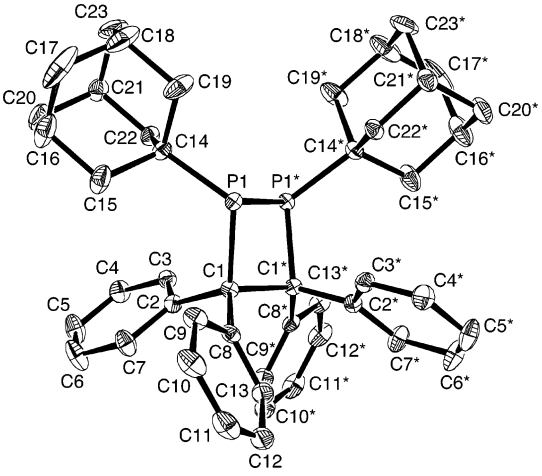
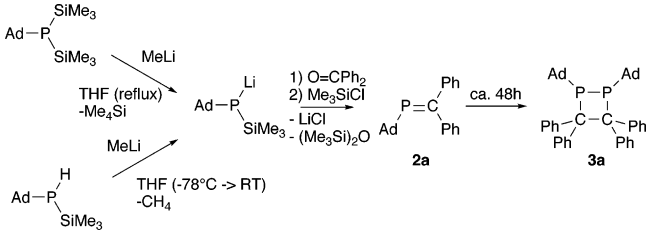


Figure 5. Molecular structure of ($AdPCPh_2$)$_2$ (**3a**). The structure contains THF of crystallization. The THF and all hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): P(1)−P(1)* 2.1888(8), P(1)−C(1) 1.9452(15), C(1)−C(1)* 1.622(3), P(1)−C(14) 1.8929(16); C(1)−P(1)−P(1)* 79.04(4), P(1)−C(1)−C(1)* 94.93(5), C(14)−P(1)−C(1) 118.79(7), C(14)−P(1)−P(1)* 107.52(5), C(2)−C(1)−P(1) 113.41(10), C(8)−C(1)−P(1) 109.41(10), C(2)−C(1)−C(1)* 114.27(13), C(8)−C(1)−C(1)* 114.65(13), C(8)−C(1)−C(2) 109.49(12).



The molecular structure of the 1,2-diphosphetane (**3a**), formed from the dimerization of **2a**, was confirmed using X-ray crystallography (Figure 5). The [2+2] cycloaddition of phosphaalkenes is often observed when insufficient thermodynamic and/or kinetic stability is conferred to the P═C bond, although formally, the dimerization is symmetry forbidden.[1h,1m,20,28,46−49] Phosphaalkenes have been observed to dimerize with both head-to-tail (to 1,3-diphosphetanes) and head-to-head (to 1,2-diphosphetanes) regiochemistry, with head-to-tail cycloaddition being most common. However, it has been proposed that phosphaalkenes

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bearing larger P than C substituents will favor head-to-head dimerization, because the long P−P bonds and short C−C bonds in the 1,2-diphosphetane will reduce intramolecular steric repulsions better than in a 1,3-diphosphetane containing four intermediate-length P−C bonds.[47] The observed head-to-head dimerization of **2a**, which possesses bulkier P than C substituents (Ad vs Ph), is consistent with these arguments.

1,2-Diphosphetane **3a** crystallizes with a molecule of THF in the unit cell; however, there is no close contact between THF and **3a**. The two P−C units of the nonplanar P_2C_2 ring in **3a** are related by a 2-fold rotation axis, with the P-Ad substituents in an anti configuration to minimize steric repulsion. Interestingly, the ring bond lengths in **3a** (P(1)−C(1), 1.9452(15) Å; C(1)−C(1)*, 1.622(3) Å) are significantly longer than typical P−C and C−C single bonds (1.85 and 1.55 Å, respectively) and are longer than those found in the seven related compounds with 1,2-P_2C_2 rings (P−C, range 1.85−1.93 Å, average 1.90 Å; C−C, range 1.47−1.62 Å, average 1.55 Å).[43,50−56] In contrast, the P−P bond (P(1)−P(1)*, 2.1888(8) Å) is slightly shorter than a typical P−P bond (2.22 Å) and shorter than that found in other 1,2-diphosphetanes (P−P, range 2.20−2.25 Å, average 2.23 Å).[43,50−56] The exocyclic P−C_{Ad} bond (P(1)−C(14) = 1.8929(16) Å) is considerably shorter than the aforementioned endocyclic P−C bonds (P(1)−C(1), 1.9452(15) Å). Presumably, these bond lengths reflect the strain of the four-membered ring. Consistent with this notion of ring strain in **3a** are the very small ring bond angles at phosphorus (C(1)−P(1)−P1* = 79.04(4) °) and carbon (P(1)−C(1)−C(1)* = 94.93(5) °).

Given that **2a** dimerizes readily, we attempted to prepare P-adamantyl phosphaalkenes bearing varying degrees of steric bulk at carbon with the objective of finding an isolable species. The success of each reaction was measured by monitoring each reaction using ^{31}P NMR spectroscopy; the spectroscopic data are shown in Table 3. In two instances, **2b** and **2c**, phosphaalkenes were detected; however, these species rapidly decomposed or self-oligomerized during attempted purification. Attempts to prepare phosphaalkene **2d** bearing bulky C-^{t}Bu substituents were unsuccessful, as AdP(Li)$SiMe_3$ did not react with this very hindered ketone.

We conclude that P-adamantyl phosphaalkenes bearing solely C-aryl or C-alkyl substituents will be difficult to isolate at ambient temperature. To the best of our knowledge, the only isolable P-adamantyl phosphaalkene is the C-heteroatom-substituted [AdP═C(OSiMe_3)^{t}Bu],[57] which was prepared using the Becker reaction (Scheme 1, path **A**). On the basis of the fact that **1a** (P-Mes) is isolable and **2a** (P-Ad) readily dimerizes to **3a**, it is tempting to conclude that the π-conjugation between the Mes group and the P═C bond is a key factor in the higher stability of **1a** compared to that of **2a**. In addition, Mes may provide better steric protection to the P═C bond than Ad. In contrast, the opposite trend in stability is observed for phosphaalkynes; namely, AdC≡P can be stored indefinitely at ambient temperature,[58] whereas MesC≡P decomposes slowly at 25 °C.[9b] These observations reinforce the delicate balance of steric and electronic factors that affect the stability of low-coordinate phosphorus compounds.

Summary

We have shown that the base-catalyzed phospha-Peterson reaction is a general and convenient synthetic route to P-mesityl phosphaalkenes bearing C-aryl substituents. These compounds have been thoroughly characterized, and ^{31}P NMR spectroscopic analysis of *E*-**1e** suggests that a facile thermal or photochemical *E*/*Z* isomerization occurs in solution. Interestingly, the X-ray crystal structures of **1b**, *E*-**1e**, and *E*-**1f** are consistent with some π-conjugation between the P═C bond and the aryl substituents. Attempts to extend the base-catalyzed phospha-Peterson reaction to the preparation of P-adamantyl phosphaalkenes were unsuccessful, as the intermediate phosphaalkenes were observed to self-oligomerize on workup. In one instance, a 1,2-diphosphetane dimer (**3a**) was isolated and structurally characterized.

The P-mesityl phosphaalkenes reported herein are attractive monomers for addition polymerization studies. In addition, the 2-pyridyl-substituted phosphaalkene (*E*-**1f**) is of considerable interest as a chelating ligand for transition metals. These investigations are currently underway and will be reported separately.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canada Foundation for Innovation (CFI), and the British Columbia Knowledge and Development Fund

(45) When hindered phosphines bearing Ad-substituents are employed as ligands in transition-metal-catalyzed reactions (i.e., Sonogashira, amination, Suzuki coupling) high activities are often observed. For recent work showing the utility of Ad-phosphines in catalysis, see: (a) Stambuli, J. P.; Bühl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9346. (b) Stambuli, J. P.; Kuwano, R.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 4746. (c) Köllhofer, A.; Pullmann, T.; Plenio, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1056. (d) Zapf, A.; Ehrentraut, A.; Beller, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4153. Rataboul, F.; Zapf, A.; Jackstell, R.; Harkal, S.; Riermeier, T.; Monsees, A.; Dingerdissen, U.; Beller, M. *Chem.—Eur. J.* **2004**, *10*, 2983.
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Supporting Information Available: X-ray crystallographic data are available as cif files. This material is available free of charge via the Internet at http://pubs.acs.org.

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