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A Convenient Synthesis of New Isolable Phosphaalkenes Using the Base-Induced Rearrangement of Secondary Vinylphosphines

Mandy Yam, Chi-Wing Tsang, and Derek P. Gates*

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1

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The secondary vinylphosphines $Ar_FP(H)C(R)=CH_2$ [**2a**, $Ar_F = 2,6\text{-}(CF_3)_2C_6H_3$, $R = CH_3$; **2b**, $Ar_F = 2,6\text{-}(CF_3)_2C_6H_3$, $R = C_6H_5$; **2c**, $Ar_F = 2,4,6\text{-}(CF_3)_3C_6H_2$, $R = CH_3$] were prepared by treating the corresponding dichlorophosphine Ar_FPCl_2 (**1**) with $H_2C=C(R)MgBr$. In the presence of catalytic base (DBU or DABCO) the vinylphosphines (**2a**–**c**) undergo quantitative 1,3-hydrogen migration over 3 d to give stable and isolable phosphaalkenes $Ar_FP=C(R)CH_3$ (**3a**, $Ar_F = 2,6\text{-}(CF_3)_2C_6H_3$, $R = CH_3$; **3b**, $Ar_F = 2,6\text{-}(CF_3)_2C_6H_3$, $R = C_6H_5$; **3c**, $Ar_F = 2,4,6\text{-}(CF_3)_3C_6H_2$, $R = CH_3$). Under analogous conditions, only 90% conversion is observed in the base-catalyzed rearrangement of $MesP(H)C(CH_3)=CH_2$ to $MesP=C(CH_3)_2$. Presumably, the increase in acidity of the P–H group when electron-withdrawing groups are employed (i.e. **2a**–**c**) favors quantitative rearrangement to the phosphaalkene tautomer (**3a**–**c**). Thus, the double-bond migration reaction is a convenient and practical method of preparing new phosphaalkenes with *C*-methyl substituents.

Introduction

As the field of low-coordinate phosphorus chemistry matures, research in phosphaalkenes ($RP=CR_2$) continues to thrive as applications are envisaged for compounds possessing a phosphorus−carbon double bond.[1] Recently, compounds with P=C bonds have successfully been employed as ligands in transition-metal-catalyzed organic reactions,[2] and they are beginning to attract attention in the synthesis of new inorganic polymers.[3−5] We are interested in the addition polymerization of P=C bonds, by analogy with olefin polymerization, as a route to new functional poly(methylenephosphines) and have recently reported the polymerization of $MesP=CPh_2$.[4] To explore the generality of this polymerization reaction and study structure−property relations in the polymers, convenient methods for the preparation of isolable monomers (i.e. phosphaalkenes) with a range of substituents are desired. Of particular interest to us are *C*-alkyl substituents (i.e. Me) because they may give more flexible polymers than fully aryl-substituted systems. However, the synthesis of stable, isolable *C*-alkyl phosphaalkenes usually requires very large (i.e. Mes* = 2,4,6-tri-*tert*-butylphenyl) and/or π-delocalizing (i.e. NR_2, $OSiMe_3$) substituents which might hinder polymerization.[1,6]

We viewed the known rearrangement of secondary vinylphosphines to phosphaalkenes (eq 1), a phosphorus analogue of the well-known allylic tautomerization (double-bond migration) in olefins (eq 2), as a potentially convenient method to prepare phosphaalkenes with *C*-methyl substituents. It is known that the double bond migration can occur in $XP(H)C(Y)=CH_2$ (X = Me, Ph, Mes; Y = H or Me) using thermolysis or catalytic base to initiate the 1,3-hydrogen migration.[7,8] However, 1,3-hydrogen migration has not proven to be a viable synthetic route to isolable

* Author to whom correspondence should be addressed: E-mail: dgates@chem.ubc.ca. Tel: 604-822-9117. Fax: 604-822-2847.

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phosphaalkenes.[9] For example, it has only afforded transient phosphaalkenes (X = CH_3 or Ph; Y = H) of low kinetic stability which were trapped chemically[8] or gave inseparable mixtures of secondary vinylphosphine and phosphaalkene when larger kinetically stabilizing substituents were employed.[7,10] We speculated that with an electron-withdrawing substituent at phosphorus the phosphaalkene tautomer might be more strongly favored over the vinylphosphine, and therefore give an isolable phosphaalkene.

$$XP(H)C(Y)=CH_2 \rightleftharpoons XP=C(Y)CH_3 \quad (1)$$

$$XCH_2C(Y)=CH_2 \rightleftharpoons XHC=C(Y)CH_3 \quad (2)$$

The 2,6-bis(trifluoromethyl)phenyl and 2,4,6-tris(trifluoromethyl)phenyl (Ar_F) substituents are formally "mesityl analogues", and they have been used extensively in the chemistry of group 15 elements.[11−23] In low-coordinate phosphorus chemistry, Ar_F groups have been employed in the synthesis of stable diphosphenes ($Ar_FP=PAr_F$),[11−13] iminophosphines ($Ar_FP=NAr_F$),[14] crystalline phosphenium salts ($Ar_FPNR_2^+$),[15] and phosphides (Ar_FPR^-).[16,17] These fluoroaryl groups are able to stabilize low-coordinate phosphorus compounds due to their moderate steric bulk (between Mes and Mes*), electron-withdrawing abilities, and the weak donor properties of the *ortho*-CF_3 groups in combination with the resistance of the C−F bonds to insertion reactions. We became interested in using Ar_F groups for phosphaalkenes after observing the intramolecular C−H activation of the Mes* group (Mes* = 2,4,6-$^tBu_3C_6H_2$−) by a transient phosphenium ion in the attempted polymerization of the phosphaalkene $Mes^*P=CH_2$ with Lewis and protic acids.[24] Surprisingly, there are only a few published phosphaalkenes containing the 2,4,6-$(CF_3)_3C_6H_2$− group [$Ar_FP=CCl_2$, $Ar_FP=C(SiMe_3)H$, $Ar_FP=C(H)Ph$][25] and, to our knowledge, no phosphaalkenes have been isolated containing the more economical 2,6-$(CF_3)_2C_6H_3$− substituent.

Herein, we report a simple method to access stable and isolable fluoroaryl-substituted phosphaalkenes with methyl groups at carbon by quantitative base-induced rearrangement of secondary vinylphosphines.

Experimental Section

General Procedures. Manipulations of air-sensitive compounds were performed under nitrogen either in an Innovative Technology glovebox or using Schlenk techniques. Hexanes, diethyl ether, and dichloromethane were dried by passing through activated alumina columns.[26] THF (from sodium/benzophenone), $CDCl_3$ (from P_2O_5), and *N*,*N*′,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (from Na) were freshly distilled prior to use. $H_2C=C(Me)Br$ and $H_2C=C(Ph)Br$ were purchased from Aldrich and distilled prior to use. 1,3-$(CF_3)_2C_6H_4$, 1,3,5-$(CF_3)_3C_6H_3$, DABCO and DBU were purchased from Aldrich and degassed prior to use. Powdered Mg was purchased from Strem and used as received. Stock solutions of Grignard reagents $H_2C=C(Me)MgBr$ and $H_2C=C(Ph)MgBr$ were freshly prepared at room temperature using powdered Mg in THF.

^1H, ^{31}P, ^{13}C, and ^{19}F NMR spectra were recorded at room temperature on a Bruker Avance 300 MHz spectrometer. Chemical shifts are reported relative to the following: residual $CHCl_3$ (δ = 7.24 for ^1H); $CDCl_3$ (δ = 77.0 for ^{13}C); 85% H_3PO_4 as an external standard (δ = 0 for ^{31}P); $CFCl_3$ in $CDCl_3$ as an external standard (δ = 0 for ^{19}F). Mass spectra were acquired using a Kratos MS 50 instrument. Elemental analyses were performed by Mr. Minaz Lakha in the Departmental Microanalysis Facility.

Preparation of 2,6-$(CF_3)_2C_6H_3PCl_2$ (1: R_1 = H). A modification of the literature procedures was followed to prepare 2,6-$(CF_3)_2C_6H_3PCl_2$ (**1**: R_1 = H).[11] We used $ClP(NEt_2)_2$ instead of PCl_3. To a solution of 1,3-$(CF_3)_2C_6H_4$ (20.0 g, 93.4 mmol) and TMEDA (11.0 mL, 73 mmol) in Et_2O (100 mL) was added *n*-BuLi (80 mL, 1.6 M, 130 mmol) at 0 °C. This solution was warmed to room temperature and stirred for 30 min and subsequently was cooled to −78 °C, where $ClP(NEt_2)_2$ (20.0 g, 95 mmol) was added dropwise. Analysis of an aliquot removed from the reaction mixture by ^{31}P NMR spectroscopy showed 2,6-$(CF_3)_2C_6H_3P(NEt_2)_2$ (δ = 115). After solvent removal, the product was extracted into hexanes (3 × 100 mL), the solution was filtered, and the hexanes and remaining 1,3-$(CF_3)_2C_6H_4$ were removed in vacuo. The liquid was redissolved in CH_2Cl_2 (150 mL), and the solution was slowly purged with HCl(g) (ca. 30 min). The solvent was removed in vacuo, the product was extracted into hexanes (3 × 50 mL) and filtered, and the hexanes was removed in vacuo. The product was purified by vacuum distillation (bp = 52 °C, 0.1 mmHg). Yield: 8.68 g (30%).

^{31}P NMR ($CDCl_3$): δ 149.0 (sept, $^4J_{PF}$ = 61 Hz). ^{19}F NMR ($CDCl_3$): δ −53.5 (d, $^4J_{FP}$ = 61 Hz). ^1H NMR ($CDCl_3$): δ 8.05 (d, $^3J_{HH}$ = 8 Hz, 2H, *m*-Ar), 7.81 (t, $^3J_{HH}$ = 8 Hz, 1H, *p*-Ar).

Preparation of 2,4,6-$(CF_3)_3C_6H_2PCl_2$ (1: R_1 = CF_3). A modification of the literature procedures were followed to prepare 2,4,6-$(CF_3)_3C_6H_2PCl_2$ (**1**: R_1 = CF_3).[12] We used $ClP(NEt_2)_2$ instead of PCl_3. To a solution of 1,3,5-$(CF_3)_3C_6H_3$ (1.00 g, 3.54 mmol) in Et_2O (20 mL) was added *n*-BuLi (2.4 mL, 1.6 M, 3.9 mmol) at 0

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°C. This solution was warmed to room temperature and was stirred for 30 min and subsequently was cooled to −78 °C, where ClP(NEt$_2$)$_2$ (1.8 g, 8.6 mmol) was added dropwise. Analysis of an aliquot removed from the reaction mixture by ^{31}P NMR spectroscopy showed 2,4,6-(CF$_3$)$_3$C$_6$H$_2$P(NEt$_2$)$_2$ (δ = 115). After solvent removal, the product was extracted into hexanes (3 × 20 mL), the solution was filtered, and the hexanes and remaining 1,3,5-(CF$_3$)$_3$C$_6$H$_3$ were removed in vacuo. The liquid was redissolved in CH$_2$Cl$_2$ (50 mL), and the solution was slowly purged with HCl(g) (ca. 15 min). The solution was filtered and the solvent was removed in vacuo. The product was purified by vacuum distillation (bp = 45 °C, 0.01 mmHg). Yield: 0.78 g (57%).

^{31}P NMR (CDCl$_3$): δ 146.1 (sept, $^4J_{PF}$ = 61 Hz). ^{19}F NMR (CDCl$_3$): δ −53.7 (d, $^4J_{PF}$ = 61 Hz, 6F, *o*-CF$_3$), −64.5 (s, 3F, *p*-CF$_3$). ^{1}H NMR (CDCl$_3$): δ 8.28 (s, *m*-Ar).

Preparation of 2,6-(CF$_3$)$_2$C$_6$H$_3$P(H)C(Me)═CH$_2$ (2a). To a cooled (−80 °C) solution of 2,6-(CF$_3$)$_2$C$_6$H$_3$PCl$_2$ (5.0 g, 16 mmol) in a mixture of diethyl ether (50 mL) and hexanes (10 mL) was added dropwise H$_2$C═C(Me)MgBr (32 mL, 0.5 M, 16 mmol). The reaction mixture was checked by ^{31}P NMR to confirm the quantitative formation of 2,6-(CF$_3$)$_2$C$_6$H$_3$PCl(C(Me)═CH$_2$) (δ = 76). LiAlH$_4$ (0.60 g, 16 mmol) was added as a slurry in ether at −80 °C, the slurry was warmed to room temperature, and subsequently H$_2$O was added to quench excess LiAlH$_4$. The water layer was extracted with fresh Et$_2$O (×2). The ether layers were combined and dried with MgSO$_4$, and solvent was removed by distillation at 1 atm. The product was distilled (bp = 35 °C, 0.01 mmHg). Yield = 3.5 g (77%).

^{31}P NMR (CDCl$_3$): δ −57.9 (d, $^1J_{PH}$ = 233 Hz). ^{19}F NMR (CDCl$_3$): δ −57.8 (d, $^4J_{PF}$ = 27 Hz). ^{1}H NMR (CDCl$_3$): δ 7.94 (d, $^3J_{HH}$ = 8 Hz, 2H, *m*-Ar), 7.58 (t, $^3J_{HH}$ = 8 Hz, 1H, *p*-Ar), 5.38 (d, $^3J_{PH}$ = 30 Hz, 1H, C═C*H*H), 5.11 (d, $^1J_{PH}$ = 231 Hz, 1H, P*H*), 4.93 (d, $^3J_{PH}$ = 13 Hz, 1H, C═CH*H*), 1.83 (d, $^3J_{PH}$ = 8 Hz, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 140.4 (d, $^1J_{PC}$ = 17 Hz, *i*-Ar), 136.3 (qd, $^2J_{CP}$ = 8 Hz, $^1J_{CF}$ = 30 Hz, *o*-Ar), 134.2 (d, $^1J_{CP}$ = 41 Hz, P−*C* = C), 130.0 (d, $^3J_{PC}$ = 6 Hz, *m*-Ar), 129.2 (s, *p*-Ar), 123.7 (q, $^1J_{CF}$ = 275 Hz, *C*F$_3$), 123.2 (d, $^2J_{PC}$ = 25 Hz, P−C = *C*), 23.7 (d, $^2J_{PC}$ = 12 Hz, *C*H$_3$).

Preparation of 2,6-(CF$_3$)$_2$C$_6$H$_3$P(H)C(Ph)═CH$_2$ (2b). To a solution of 2,6-(CF$_3$)$_2$C$_6$H$_3$PCl$_2$ (3.0 g, 9.5 mmol) in Et$_2$O (20 mL) was added H$_2$C═C(Ph)MgBr (30 mL, 0.317 M, 9.5 mmol). After being stirred for 1 h, the solution turned yellow and a white precipitate formed. The reaction was checked by ^{31}P NMR to confirm the formation of 2,6-(CF$_3$)$_2$C$_6$H$_3$PCl(C(Ph)═CH$_2$) (δ = 71). A slurry of LiAlH$_4$ (0.18 g, 4.7 mmol) in Et$_2$O (5 mL) was added at 0 °C. After the mixture was warmed to room temperature and excess LiAlH$_4$ quenched with water (10 mL), the organic layer was dried with MgSO$_4$ and filtered and the solvent removed in vacuo. The liquid product was distilled (bp = 104 °C, 0.01 mmHg) and subsequently recrystallized from a minimal amount of hexanes at −70 °C. Yield = 1.54 g (47%).

^{31}P NMR (CDCl$_3$): δ −61.5 (d, $^1J_{PH}$ = 235 Hz). ^{19}F NMR (CDCl$_3$): δ −58.2 (d, $^4J_{FP}$ = 27 Hz). ^{1}H NMR (CDCl$_3$): δ 7.99 (d, $^3J_{HH}$ = 8 Hz, 2H, *m*-Ar), 7.64 (t, $^3J_{HH}$ = 8 Hz, 1H, *p*-Ar), 7.42−7.27 (m, 5H, Ph), 5.64 (dd, $^3J_{PH}$ = 17 Hz, $^2J_{HH}$ = 2 Hz, 1H, C═C*H*H), 5.35 (d sept, $^1J_{PH}$ = 235 Hz, $^5J_{FH}$ = 2 Hz, 1H, P*H*), 4.67 (dd, $^3J_{PH}$ = 7 Hz, $^2J_{HH}$ = 2 Hz, 1H, C═CH*H*).

Preparation of 2,4,6-(CF$_3$)$_3$C$_6$H$_2$P(H)C(Me)═CH$_2$ (2c). To a solution of 2,4,6-(CF$_3$)$_3$C$_6$H$_2$PCl$_2$ (0.78 g, 2.0 mmol) in a mixture of Et$_2$O (20 mL) and hexanes (10 mL) was added dropwise H$_2$C═C(Me)MgBr (4.9 mL, 0.5 M, 2.4 mmol) in Et$_2$O. The reaction was checked by ^{31}P NMR, and 2,4,6-(CF$_3$)$_3$C$_6$H$_2$PCl(C(Me)═CH$_2$) (δ = 75) was formed quantitatively. LiAlH$_4$ (0.04 g, 1.05 mmol) was added as a slurry in ether at −80 °C, and the mixture was warmed to room temperature. Subsequently the ether layer was extracted with H$_2$O to quench excess LiAlH$_4$ and dried with MgSO$_4$ and the solvents were removed at 1 atm. The liquid product was distilled (bp = 35 °C, 0.01 mmHg). Yield = 0.50 g (70%).

^{31}P NMR (CDCl$_3$): δ −54.9 (d, $^1J_{PH}$ = 231 Hz). ^{19}F NMR (CDCl$_3$): δ −58.6 (d, $^4J_{FP}$ = 26 Hz, 6F, *o*-CF$_3$), −64.2 (s, 3F, *p*-CF$_3$). ^{1}H NMR (CDCl$_3$): δ 8.12 (s, 2H, *m*-Ar), 5.43 (d, $^3J_{PH}$ = 34 Hz, 1H, C═C*H*H), 5.12 (d, $^1J_{PH}$ = 231 Hz, 1H, P−H), 5.02 (d, $^3J_{PH}$ = 14 Hz, 1H, C═CH*H*), 1.79 (d, $^3J_{PH}$ = 7 Hz, 3H, C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 140.2 (d, $^1J_{CP}$ = 46 Hz, P−*C*═C), 139.3 (d, $^1J_{CP}$ = 17 Hz, *i*-Ar), 137.4 (qd, $^2J_{CF}$ = 31 Hz, $^2J_{PC}$ = 8 Hz, *o*-Ar), 131.6 (q, $^2J_{CF}$ = 34 Hz, *p*-Ar), 126.8 (s, *m*-Ar), 125.2 (d, $^2J_{PC}$ = 29 Hz, P−C═*C*), 123.0 (q, $^1J_{CF}$ = 275 Hz, *o*-CF$_3$), 122.6 (q, $^1J_{CF}$ = 273 Hz, *p*-CF$_3$), 24.0 (d, $^2J_{CP}$ = 9 Hz, CH$_3$).

Preparation of 2,6-(CF$_3$)$_2$C$_6$H$_3$P═CMe$_2$ (3a). To a solution of 2,6-(CF$_3$)$_2$C$_6$H$_3$P(H)C(Me)═CH$_2$ (**2a**) (3.5 g, 12.2 mmol) in CH$_2$Cl$_2$ (20 mL) was added DBU (0.1 g, 0.6 mmol). The solution was stirred for 3 d and the reaction progress monitored by ^{31}P NMR. Upon complete consumption of **2a** the reaction mixture was extracted with degassed H$_2$O (3 × 10 mL) to remove DBU, dried with MgSO$_4$, and filtered and the solvent removed under N$_2$ (1 atm). The product was distilled (bp = 35 °C, 0.01 mmHg). Yield = 3.1 g (89%).

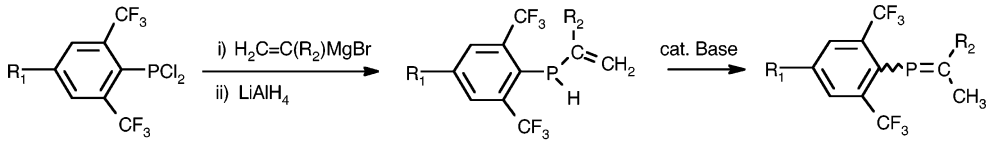
^{31}P NMR (CDCl$_3$): δ 196.0 (m). ^{19}F NMR (CDCl$_3$): δ −59.6 (d, $^4J_{PF}$ = 22 Hz). ^{1}H NMR (CDCl$_3$): δ 7.90 (d, $^3J_{HH}$ = 8 Hz, 2H, *m*-Ar), 7.55 (t, $^3J_{HH}$ = 8 Hz, 1H, *p*-Ar), 2.25 (d, $^3J_{PH}$ = 25 Hz, 3H, ═CC*H*$_3$), 1.72 (d, $^3J_{PH}$ = 13 Hz, 3H, ═CC*H*$_3$,). ^{13}C NMR (CDCl$_3$): δ 193.2 (d, $^1J_{PC}$ = 42 Hz, P═*C*), 141.8 (d, $^1J_{PC}$ = 74 Hz, *i*-Ar), 134.5 (q, $^2J_{CF}$ = 29 Hz, *o*-Ar), 129.0 (d, $^3J_{PC}$ = 5 Hz, *m*-Ar), 128.2 (s, *p*-Ar), 123.6 (q, $^1J_{CF}$ = 275 Hz, CF$_3$), 27.9 (d, $^2J_{PC}$ = 47 Hz, CH$_3$), 27.1 (d, $^2J_{PC}$ = 17 Hz, CH$_3$). MS (EI, 70 eV): 287, 286 [3, 24; M$^+$]; 272, 271 [11, 100; M$^+$ − CH$_3$]. Anal. Calcd for C$_{11}$H$_9$F$_6$P: C, 46.17; H, 3.17. Found: C, 46.49; H, 3.13.

Preparation of (*E*,*Z*)-2,6-(CF$_3$)$_2$C$_6$H$_3$P═C(Ph)(CH$_3$) (3b). To a solution of 2,6-(CF$_3$)$_2$C$_6$H$_3$P(H)C(Ph)═CH$_2$ (**2b**) (1.54 g, 4.42 mmol) in CH$_2$Cl$_2$ (5 mL) was added DBU (0.10 g, 0.6 mmol). The solution turned slightly yellow, and the quantitative formation of **3b** was observed over 3 d as determined by ^{31}P NMR. The reaction mixture was extracted with degassed water (3 × 15 mL) to remove DBU, the organic layer was dried with MgSO$_4$ and filtered, and the solvent was removed in vacuo. The product was distilled (bp = 113 °C, 0.01 mmHg). Yield = 0.88 g (57%).

^{31}P NMR (CDCl$_3$): δ 209.3 (>99%; *E*-isomer, tentative), 200.7 (<1%; *Z*-isomer). ^{19}F NMR (CDCl$_3$): δ − 59.5 (d, $^4J_{FP}$ = 20 Hz). ^{1}H NMR (CDCl$_3$): δ 7.97 (d, $^3J_{HH}$ = 8 Hz, 2H, *m*-Ar), 7.67 (m, 2H, *o*-Ph), 7.62 (t, $^3J_{HH}$ = 8 Hz, 1H, *p*-Ar), 7.41−7.36 (m, 3H, *m*,*p*-Ph), 2.13 (d, $^3J_{PH}$ = 14 Hz, 3H, C*H*$_3$). ^{13}C NMR (CDCl$_3$): 193.3 (d, $^1J_{PC}$ = 41 Hz, P═*C*), 143.5 (d, $^2J_{PC}$ = 27 Hz, *i*-Ph), 141.7 (d, $^2J_{PC}$ = 74 Hz, *i*-Ar), 134.6 (q, $^2J_{CF}$ = 30 Hz, *o*-Ar), 129.6, 129.2 (d, $^{3/4}J_{PC}$ = 5 Hz; d, $^{3/4}J_{PC}$ = 4 Hz; *m*-Ph and Ar), 128.9, 128.5 (s, *p*-Ph and Ar), 125.3 (d, $^3J_{PC}$ = 21 Hz, *o*-Ph), 123.7 (q, $^1J_{FC}$ = 275 Hz, *C*F$_3$), 25.4 (d, $^2J_{PC}$ = 16 Hz, *C*H$_3$). MS (EI, 70 eV): 349, 348 [16, 88; M$^+$]; 334, 333 [16, 100; M$^+$ − CH$_3$]; 271 [36, M$^+$ − Ph]; 103 [50; M$^+$ − PAr]. Anal. Calcd for C$_{16}$H$_{11}$F$_6$P: C, 55.19; H, 3.18. Found: C, 55.42; H, 3.01.

Preparation of 2,4,6-(CF$_3$)$_3$C$_6$H$_2$P═CMe$_2$ (3c). This reaction was performed on an NMR scale. In an NMR tube, DABCO (1.0 mg, 0.01 mmol) was mixed with **2c** (0.10 g; 0.28 mmol) in THF (1 mL). Compound **3c** was formed quantitatively over 3 d as determined by ^{31}P NMR. The solvent was removed in vacuo, and the liquid residue was dissolved in CH$_2$Cl$_2$ (2 mL) and extracted with water. The CH$_2$Cl$_2$ solution was dried with MgSO$_4$ and filtered,

Scheme 1



1 **2a** (R_1=H; R_2=CH_3) **2b** (R_1=H; R_2=Ph) **2c** (R_1=CF_3; R_2=CH_3) **3a-c**

and the solvent was removed leaving a small amount of **3c** as a colorless liquid. An isolated yield was not determined.

^{31}P NMR ($CDCl_3$): δ 191.9 (m). ^{19}F NMR ($CDCl_3$): δ −60.2 (d, $^4J_{PF}$ = 22 Hz, 6F, *o*-CF_3), −64.0 (s, 3F, *p*-CF_3). ^{1}H NMR ($CDCl_3$): δ 8.13 (s, 2H, *m*-Ar), 2.28 (d, $^3J_{PH}$ = 25 Hz, 3H, =CCH_3,), 1.75 (d, $^3J_{PH}$ = 13 Hz, 3H, =CCH_3).

Results and Discussion

Dichlorophosphine **1** (R_1 = H) can be prepared conveniently by direct lithiation of 1,3-bis(trifluoromethyl)benzene with *n*-BuLi/TMEDA and subsequent reaction with PCl_3,[11] or to prevent multiple substitution at phosphorus, we prefer to use the protected phosphine $ClP(NEt_2)_2$ followed by deprotection with anhydrous HCl. We observed a single product, **1** (R_1 = H), which resulted from selective lithiation in the 2-position of 1,3-$(CF_3)_2C_6H_4$. The dichlorophosphine was treated with freshly prepared isopropenylmagnesium bromide (1 equiv) in a mixture of ether/hexanes (5:1). The quantitative formation of 2,6-$(CF_3)_2C_6H_3PCl(C(Me)=CH_2)$ was confirmed by ^{31}P NMR spectroscopy (δ = 76) of an aliquot from the reaction mixture. To simplify the synthetic procedure, we did not isolate the chlorophosphine and it was reduced in the same pot to secondary vinylphosphine **2a** using $LiAlH_4$ (Scheme 1). No problems were encountered by combining these two steps. The success of the reduction reaction was confirmed by ^{31}P NMR spectroscopic analysis of the crude reaction mixture, which showed the clean formation of **2a** (δ = −57.9, $^1J_{PH}$ = 233 Hz). Secondary vinylphosphine **2a** was isolated as a colorless liquid (yield = 77%) after vacuum distillation (bp = 35 °C; 0.01 mmHg). The compound was fully characterized by using ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.

Vinylphosphine **2a** is stable in its pure form when kept at room temperature under an inert atmosphere. However, after the addition of a trace of DBU (5%) to a solution of **2a** in CH_2Cl_2, the partial formation of phosphaalkene **3a** was detected by ^{31}P NMR (δ = 196). Remarkably, after 3 d the 1,3-hydrogen migration was complete and the phosphaalkene **3a** was the only species detected in the ^{31}P NMR spectrum of the reaction mixture. The purification of **3a** initially proved challenging since DBU was always found in the product after vacuum distillation. Interestingly, we found that the DBU could be removed by extraction of the crude reaction mixture in CH_2Cl_2 with degassed H_2O. Remarkably, no decomposition of **3a** in the presence of degassed water was observed. Subsequent drying of the CH_2Cl_2 layer with $MgSO_4$ and removal of the solvent afforded analytically pure **3a** (isolated yield = 89%) as a colorless liquid after vacuum distillation (bp = 35 °C; 0.01 mmHg).

To test the generality of this novel route to *P*-fluoroaryl phosphaalkenes with *C*-methyl substituents, we prepared secondary vinylphosphines **2b**,**c** by following procedures similar to those used for **2a**. In each case, the vinyl substitution and subsequent reduction with $LiAlH_4$ could be performed conveniently in one pot. The presence of doublet resonances in the ^{31}P NMR spectra of the reaction mixtures confirmed that the secondary vinylphosphines **2b**,**c** had been formed quantitatively (**2b**, δ = −61.5, $^1J_{PH}$ = 235 Hz; **2c**, δ = −54.9, $^1J_{PH}$ = 231 Hz). Both of the compounds were isolated by vacuum distillation and fully characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy. In the presence of base (DBU or DABCO), each secondary vinylphosphine tautomerized quantitatively to yield phosphaalkenes (**3b**,**c**) as determined by ^{31}P NMR spectroscopy. Compound **3b** was purified by distillation and was isolated in 57% yield. The lower isolated yield of **3b** compared with **3a** (89%) likely results from the increased losses in the distillation of the higher boiling **3b** (bp = 113 °C; 0.01 mmHg). For many synthetic purposes, **3b** could be generated in situ by quantitative rearrangement of **2b** and used without further purification. Interestingly, the ^{31}P NMR spectrum of **3b** in $CDCl_3$ showed a majority one isomer (δ = 209.3; >99%) and only a trace of a second isomer (δ = 200.7; <1%). We speculate that the major isomer is the *E*-isomer partly upon steric reasons and also in *C*-aryl-containing phosphaalkenes the *E*-isomer is usually shifted downfield with respect to the *Z*-isomer.[27] To date, we have not been able to obtain single crystals of **3b** to confirm this assignment.

All of the new phosphaalkenes synthesized (**3a**−**c**) were stable when stored under inert atmosphere, and no evidence for equilibration with their vinylphosphine tautomers was observed even after several months. It is interesting that the fluoroaryl secondary vinylphosphines (**2a**−**c**) rearrange quantitatively to phosphaalkenes (**3a**−**c**), while only partial conversion to phosphaalkene is observed with Mes-P(H)C(Me)=CH_2. Mathey and co-workers reported 80−90% conversion of MesP(H)C(Me)=CH_2 to MesP=CMe_2 by thermal-induced rearrangement (100 °C), and the reaction was believed to follow either a concerted or radical pathway.[7,28] We have repeated this reaction with catalytic base (5% DBU) and have obtained similar conversions (ca. 90% MesP=CMe_2). Unfortunately, the vinylphosphine and phosphaalkene are inseparable by distillation, and therefore, this

(27) For a compilation of ^{31}P NMR chemical shifts for phosphaalkenes, see: Lochschmidt, S.; Schmidpeter, A. *Phosphorus Sulfur* **1986**, *29*, 73.

(28) For a theoretical study, see: Nguyen, M. T.; Landuyt, L.; Vanquickenborne, L. G. *Chem. Phys. Lett.* **1993**, *212*, 543.

route cannot be used to synthesize phosphaalkenes bearing the mesityl group. Through the synthesis of **3a**−**c** free of **2a**−**c**, we have demonstrated that double-bond migration is indeed a viable method to prepare phosphaalkenes with electron-withdrawing substituents at phosphorus. The fluoroaryl substituents likely cause the phosphaalkene tautomer (**3**) to be favored by increasing the acidity of the P−H proton in **2** relative to when the mesityl group is used. An indication of the increased acidity of the P−H proton in **2** can be obtained from the proton chemical shifts of **2a**−**c** (5.11−5.35 ppm), which are greatly shifted downfield from that of MesP(H)C(Me)=CH_2 (4.75 ppm).[7] Moreover, recent calculations have shown that the acidity of the phosphine Ar_F-PH_2 [Ar_F = 2,6-$(CF_3)_2C_6H_3$] is significantly higher than that for $PhPH_2$.[29] The higher acidity for Ar_FPH_2 was attributed to (i) increased stablilization of the conjugate base (i.e. Ar_FPH^- is more stable than $PhPH^-$) through interaction of the lone pair on phosphorus with the aromatic system and (ii) destabilizing repulsions between the phosphorus and fluorine lone pairs in the acid (Ar_FPH_2). Given the increase in P−H acidity when electron-withdrawing substituents at phosphorus are employed, it should therefore be possible to prepare a range of new phosphaalkenes from suitably substituted secondary vinylphosphines.

(29) Miqueu, K.; Sotiropoulos, J.-M.; Pfister-Guillouzo, G.; Rudzevich, V.; Romanenko, V.; Bertrand, G. *Eur. J. Inorg. Chem.* **2004**, 381.

Summary

In summary, we have shown that the base-induced 1,3-hydrogen rearrangement reaction is a synthetically useful method for preparing phosphaalkenes with C−Me substituents provided electron-withdrawing groups are employed at phosphorus. This represents the first time that the 1,3-hydrogen migration reaction has been used to synthesize an isolable phosphaalkene. Furthermore, **3a**,**b** are the first examples of phosphaalkenes bearing the 2,6-bis(trifluoromethyl)phenyl group. Future studies will explore the reactivity of these new P=C monomers with potential initiators for addition polymerization.

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