

Synthesis of Functional Phosphines with Ortho-Substituted Aryl Groups: 2-RC₆H₄PH₂ and 2-RC₆H₄P(SiMe₃)₂ (*R* = 2-*i*-Pr- or 2-*t*-Bu-)

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Received 15 February 2010; revised 7 April 2010

ABSTRACT: *The synthesis and characterization of 2-*i*-PrC₆H₄PCL₂ (3), 2-*t*-BuC₆H₄PCL₂ (4), 2-*i*-PrC₆H₄PH₂ (5), 2-*t*-BuC₆H₄PH₂ (6), 2-*i*-PrC₆H₄P(SiMe₃)₂ (7), and 2-*t*-BuC₆H₄P(SiMe₃)₂ (8) are described.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:265–270, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20606

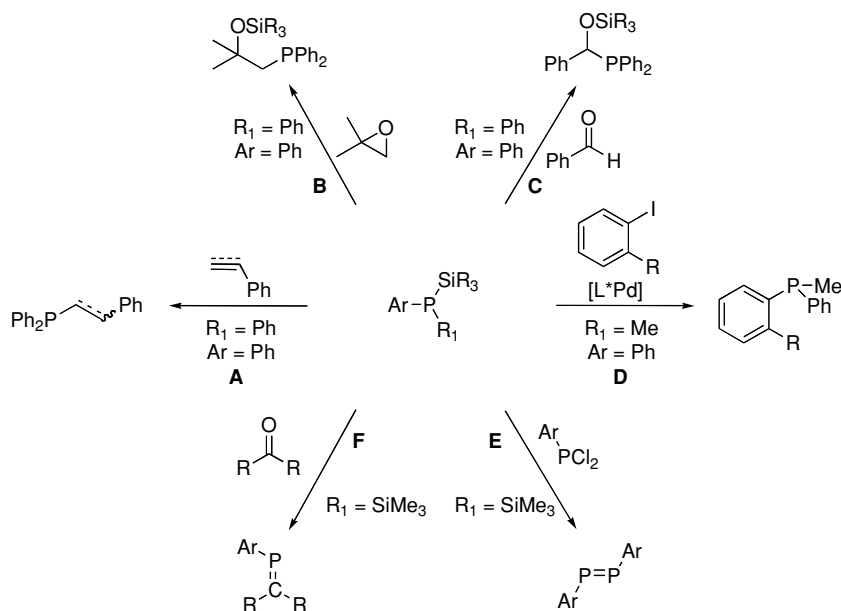
INTRODUCTION

The development of chemically functional phosphines bearing sterically encumbering substituents has had a profound impact on the low-coordinate chemistry of phosphorus. For example, the employment *P*-substituents such as 2,4,6-Me₃C₆H₂– (mesityl, Mes) and 2,4,6-*t*-Bu₃C₆H₂– (supermesityl, Mes*) permitted the isolation of the phosphaaalkene MesP=CPh₂ [1] and the diphosphene Mes*P=PMe* [2]. Recently, the development of bulkier and more sophisticated aryl substituents [e.g., 2,6-{2,4,6-(*i*-Pr)₃C₆H₂}₂C₆H₃– and 2,4,6-{CH(SiMe₃)₂}₃C₆H₂–] led to the isolable compounds of the heavier elements of the periodic table with low-coordination numbers [3].

Combining a *P*-aryl substituent with *P*-H or *P*-SiMe₃ functional groups at phosphorus results in reactive phosphines that are important building blocks in organic, main group, and organometallic chemistry [4,5]. Several representative reactions are shown in Scheme 1 to illustrate the utility of phosphines with *P*-Si functionalities. Phosphines with a single trimethylsilyl substituent may be employed to functionalize alkenes and alkynes **A** [6–12], ring-open epoxides **B** [13], add to aldehydes **C** [13–15], and support metal-catalyzed coupling reactions **D** [16–18]. In addition, bis(trimethylsilyl)phosphines are important precursors to diphosphenes **E** [19], and phosphaaalkenes **F** [20] when appropriately bulky aryl substituents (Ar) are employed.

We [21], and others [22], are interested in the development of applications for phosphaaalkenes in areas such as polymer science and catalysis (Scheme 2, **I** and **II**). We have demonstrated that a delicate balance between kinetic and thermodynamic stability is required to afford isolable but polymerizable monomers. For example, mesityl-substituted MesP=CPh₂ polymerizes [23], whereas we have been unsuccessful in polymerizing supermesityl-substituted Mes*P=CH₂ [24]. The polymerization of *P*=C bonds opens the door to the generation of a wide range of functional homopolymers, or block- or random-copolymers, that are effective in binding transition metals [25,26], forming self-assembled nanostructures, and as ligands for use

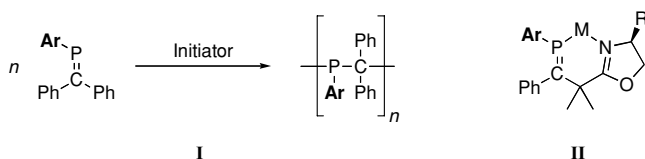
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SCHEME 1

in polymer-supported catalysts [27]. In addition, we have recently been interested in the development of phosphalkene-based ligands for use in asymmetric catalysis (Scheme 2, **II**) [28,29].

To tune the steric properties of phosphalkenes for application in catalysis and polymer science, we have been interested in the development of moderately bulky P-aryl substituents with a single substituent in the ortho-position. Since (2-MeC₆H₄)P=CPh₂ was reported to be unstable [1], we pursued the preparation of systems with the slightly larger *i*-Pr or *t*-Bu substituent in the 2-position of the aryl substituent. Herein, we report the synthesis of the new primary phosphines 2-*i*-PrC₆H₄PH₂ and 2-*t*-BuC₆H₄PH₂ as well as the bis(trimethylsilyl)phosphines 2-*i*-PrC₆H₄P(SiMe₃)₂ and 2-*t*-BuC₆H₄P(SiMe₃)₂. This synthetic methodology is amenable to the isolation of multigram quantities of material from commercially available starting materials.

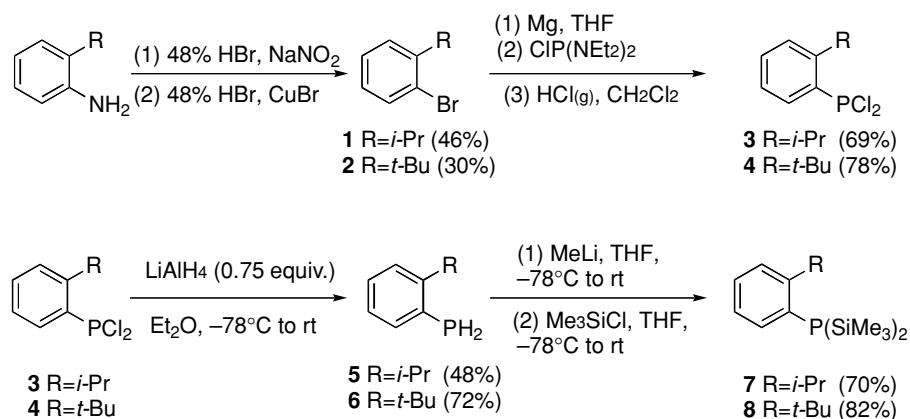


SCHEME 2

RESULT AND DISCUSSION

The synthesis starts with aryl bromides **1** and **2**, prepared from the corresponding commercially available aniline derivatives using a Sandmeyer reaction [30] (Scheme 3). The addition of magnesium metal to the aryl bromide (**1** or **2**) in tetrahydrofuran (THF) generates the respective Grignard reagents, which are then treated with ClP(NEt₂)₂ [31]. The use of diethylamino-protected chlorophosphine instead of PCl₃ ensures that only a single aryl-substitution occurs at phosphorus. Analysis of the product by ³¹P NMR spectroscopy confirms that only a single product is formed, and the chemical shift is consistent with its formulation as 2-RC₆H₄P(NEt₂)₂ (R = *i*-Pr: δ = 94; R = *t*-Bu: δ = 93). Although it is possible to isolate the bis(aminophosphines), we found it more convenient to simply treat the crude product with anhydrous hydrogen chloride in CH₂Cl₂ to remove the diethylamino protecting groups. The dichlorides **3** and **4** are obtained in satisfactory overall yields after distillation (69% and 78%, respectively). The products were analyzed by ³¹P NMR spectroscopy (**3**: δ = 164, **4**: δ = 166). These chemical shifts are similar to related dichloroarylphosphines such as MesPCl₂ (δ = 167) [32].

Reduction of the dichlorides **3** and **4** using LiAlH₄ affords primary phosphines **5** and **6** in good isolated yield (70% and 82%, respectively). Although phosphine **5** has previously been mentioned, its synthesis and characterization were not reported [33].



SCHEME 3

Analysis of the products using ^{31}P NMR spectroscopy revealed triplet resonances that are characteristic of primary phosphines [**5**: $\delta = -127$ (t, $^1J_{\text{PH}} = 203$ Hz), **6**: $\delta = -107$ ppm (t, $^1J_{\text{PH}} = 202$ Hz)]. Interestingly, these signals are shifted downfield when compared to MesPH_2 (-149 ppm, t, $^1J_{\text{PH}} = 203$ Hz) [32] and the chemical shift for **6** is closer to alkyl phosphines such as $t\text{-BuPH}_2$ (-80 ppm, t, $^1J_{\text{PH}} = 180$ Hz) and ($\text{cyclo-C}_6\text{H}_{11}$) PH_2 (-111 ppm, t, $^1J_{\text{PH}} = 187$ Hz) [32]. Compounds **5** and **6** were further characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, and mass spectrometry, each of which supported the assigned structures. Owing to the difficulty handling pyrophoric phosphines **5** and **6**, elemental microanalysis could not be accurately obtained.

The final step in the preparation of bis(trimethylsilyl)phosphines **7** and **8** involves treating **5** or **6** with MeLi (2 equiv) followed by silylation using Me_3SiCl . The desired bis(trimethylsilyl)phosphines were isolated in reasonable yield after distillation (**7**: 48%, **8**: 72%). Compound **7** and **8** were characterized by ^{31}P , ^1H , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, low-resolution and high-resolution mass spectrometry, and elemental analysis. Interestingly, the ^{31}P chemical shift of **7** ($\delta = -153$) is similar to $\text{MesP}(\text{SiMe}_3)_2$ ($\delta = -164$), whereas that for **8** ($\delta = -135$) is similar to alkyl-substituted $\text{cyclo-C}_6\text{H}_{11}\text{P}(\text{SiMe}_3)_2$ ($\delta = -139$). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **7** and **8** are consistent with the proposed structures.

SUMMARY

A synthetic methodology has been developed to prepare new moderately bulky phosphines from commercially available 2-substituted anilines. The chlorides, hydrides, and silylides of 2-*i*-PrC₆H₄- and

2-*t*-BuC₆H₄-substituted phosphines have been prepared and fully characterized spectroscopically. This synthetic route is amenable to the preparation of multigram quantities of product in a linear fashion. The new bis(trimethylsilyl)aryldichlorophosphines (**7** and **8**) are of interest for the synthesis of new phosphalkenes for applications as supporting ligands for metal-catalyzed organic transformations.

EXPERIMENTAL

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 CH_2Cl_2 were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. THF was distilled from sodium/benzophenone ketyl. Reagents, 2-*i*-PrC₆H₄NH₂, 2-*t*-BuC₆H₄NH₂, Mg, Me_3SiCl , and LiAlH_4 were purchased from Aldrich and used as received. Anhydrous HCl was obtained from BOC Gases and used as received. MeLi in Et_2O was purchased from Aldrich and titrated with *N*-benzylbenzamide prior to use.

^1H , ^{31}P , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at room temperature on Bruker Avance 300 or 400 MHz spectrometers. 85% H_3PO_4 was used as an external standard ($\delta = 0.0$ for ^{31}P). ^1H NMR spectra were referenced to residual protonated solvent, and $^{13}\text{C}\{^1\text{H}\}$ NMR were referenced to the deuterated solvent. 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).

2-*i*-PrC₆H₄PCL₂ (3). To a solution of Mg (2.97 g, 122 mmol) in THF (150 mL), 2-*i*-PrC₆H₄Br (20.3 g, 102 mmol) was added. After 30 min, the Grignard activated and the solution was refluxed for an additional 2 h. The mixture was cooled to r.t. and treated with ClP(NEt₂)₂ [31] (23.6 g, 112 mmol) and washed with THF (5 mL). The solvent was removed in vacuo, and the phosphine was extracted with hexanes (1 × 100 mL, 2 × 80 mL). The hexanes were removed in vacuo leaving crude 2-*i*-PrC₆H₄P(NEt₂)₂ as a colorless liquid with ³¹P NMR singlet resonance of 94 ppm. The crude solution of 2-*i*-PrC₆H₄P(NEt₂)₂ in CH₂Cl₂ (150 mL) was treated with gaseous dry HCl, and the mixture became darker, cloudy, and then clear. ³¹P NMR analysis of an aliquot removed from the reaction mixture indicated two signals at 221 ppm (PCl₃) and 167 ppm (2-*i*-PrC₆H₄PCL₂). CH₂Cl₂ was evaporated in vacuo. The yellow solid was extracted with toluene (3 × 60 mL), filtered, and the solvent was removed in vacuo. The crude product was purified by vacuum distillation 95°C (0.01 mmHg) to afford **3** (15.5 g, 69%) as a colorless liquid.

³¹P NMR (162 MHz, CDCl₃): δ 164 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.15–8.11 (m, 1H), 7.55–7.51 (m, 1H), 7.42–7.38 (m, 2H), 3.76 (sept, ³J_{HH} = 7 Hz, 1H), 1.36 (d, ³J_{HH} = 7 Hz, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.8 (d, J_{PC} = 31 Hz), 137.2 (d, J_{PC} = 56 Hz), 133.1, 130.6 (d, J_{PC} = 7 Hz), 127.2 (d, J_{PC} = 1 Hz), 125.7 (d, J_{PC} = 34 Hz), 31.1 (d, J_{PC} = 33 Hz), 24.4; MS (EI): *m/z* (%) 224, 222, 220 [7, 42, 66, M⁺], 209, 207, 202 [3, 15, 23, M-CH₃], 187, 186, 185 [10, 9, 32, M-Cl]; Anal Calcd for C₉H₁₁Cl₂P: C, 48.90; H, 5.02; found: C, 48.84; H, 5.02.

2-*t*-BuC₆H₄PCL₂ (4). Same procedure as described above for **3**. Used 2-*t*-BuC₆H₄Br (8.47 g, 40 mmol), Mg (1.16 g, 48 mmol), and PCl(NEt₂)₂ (9.27 g, 44 mmol). The crude product was purified by vacuum distillation 110°C (0.01 mmHg) to afford **4** (7.4 g, 78%) as a colorless liquid.

³¹P NMR (121 MHz, CDCl₃): δ 166 (s); ¹H NMR (400 MHz, CDCl₃): δ 8.36–8.31 (m, 1H), 7.46–7.36 (m, 3H), 1.57 (s, 9H); ¹³C{¹H} NMR (121 MHz, CDCl₃): δ 153.5 (d, J_{PC} = 28 Hz), 140.4 (d, J_{PC} = 68 Hz), 134.9, 132.4, 127.5, 125.2, 37.0, 33.7; HRMS (EI): Calcd for C₁₀H₁₃Cl₂P 234.0132; found: 234.0131; MS (EI): *m/z* (%) 236, 235, 234 [43, 24, 68, M⁺], 221, 220, 219 [18, 4, 27, M-Me], 201, 200, 199 [14, 10, 45, M-Cl], 147 [100, M-CH₃Cl₂], 133 [22, M-PCl₂]; Anal Calcd for C₁₀H₁₃Cl₂P: C, 51.09; H, 5.57; found: C, 50.97; H, 5.60.

2-*i*-PrC₆H₄PH₂ (5). To a cooled (–78°C) solution of LiAlH₄ (2.1 g, 56 mmol) in Et₂O (300 mL), a

solution of **3** (15.5 g, 70 mmol) in Et₂O (15 mL) was added. The cooling bath was removed, and the solution was warmed to room temperature. ³¹P NMR analysis of an aliquot removed from the reaction mixture showed triplet resonance at –129 ppm. Degassed water (100 mL) was added to quench residual aluminum hydride. (*Caution:* Extreme care should be taken when adding the first few milliliters of water since quenching is highly exothermic and H₂ is evolved.) The ether layer was removed, and the aqueous layer extracted with Et₂O (150 mL, 100 mL). The organic layers were combined, and the solvent removed in vacuo. The crude product was purified by vacuum distillation 60°C (0.01 mmHg) to afford **5** (7.5 g, 70%) as colorless liquid. (*Caution:* The product is pyrophoric and very malodorous.)

³¹P NMR (162 MHz, CDCl₃): δ –127 (t, J_{PH} = 203 Hz); ¹H NMR (400 MHz, CDCl₃): δ 7.53–7.48 (m, 1H), 7.34–7.26 (m, 2H), 7.13–7.06 (m, 1H), 3.96 (d, J_{PH} = 203 Hz, 2H), 3.28 (sept, ³J_{HH} = 7 Hz, 1H), 1.29 (d, ³J_{HH} = 7 Hz, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 152 (d, J_{PC} = 13 Hz), 136 (d, J_{PC} = 7 Hz), 129, 128 (d, J_{PC} = 8 Hz), 126 (d, J_{PC} = 3 Hz), 125 (d, J_{PC} = 3 Hz), 33 (d, J_{PC} = 15 Hz), 24; MS (EI): *m/z* (%) 153, 152 [100, 11, M⁺], 138, 137 [33, 4, M-Me], 120, 119 [13, 4, M-PH₂], 111, 110 [82, 9, M-C₃H₆], 91 [40, C₇H₇].

2-*t*-BuC₆H₄PH₂ (6). Same procedure as described above for **5**. Used **4** (7.2 g, 31 mmol) and LiAlH₄ (0.873 g, 23 mmol). The crude product was purified by vacuum distillation 60°C (0.01 mmHg) to afford title compound (4.17 g, 82%) as a colorless liquid.

³¹P NMR (162 MHz, CDCl₃): δ –107 (t, ¹J_{PH} = 202 Hz); ¹H NMR (400 MHz, CDCl₃): δ 7.58–7.53 (m, 1H), 7.47–7.42 (m, 1H), 7.29–7.23 (m, 1H), 7.11–7.05 (m, 1H), 4.21 (d, ¹J_{PH} = 203 Hz, 2H), 1.52 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 154.3 (d, J_{PC} = 15 Hz), 140.0, 128.7, 127.8 (d, J_{PC} = 17 Hz), 126.6 (d, J_{PC} = 5 Hz), 125.8, 36.9, 31.3 (d, J_{PC} = 11 Hz); HRMS calcd for C₁₀H₁₅P: 166.0911; found: 166.0908; MS (EI): *m/z* (%) 167, 166 [7, 62, M⁺], 166 [100, M-H], 152, 151 [5, 56, M-Me], 134, 133 [3, 16, M-PH₂], 110, 109 [13, 44, M-*t*-Bu], 57 [28, *t*-Bu].

2-*i*-PrC₆H₄P(SiMe₃)₂ (7). To a cooled solution (–78°C) of **5** (7.0 g, 46 mmol) in THF (100 mL), MeLi in Et₂O (1.45 M, 70 mL, 101 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 1 h whereafter the solution was cooled (–78°C) and treated with Me₃SiCl (13.5 mL, 106 mmol). ³¹P NMR analysis of an aliquot removed from the reaction mixture revealed

the presence of 2-*i*-PrC₆H₄P(SiMe₃)₂ at –153 ppm. Often, after the first lithiation a mixture of 2-*i*-PrC₆H₄P(SiMe₃)₂ and 2-*i*-PrC₆H₄PH(SiMe₃) was observed. In this instance, the reaction mixture was relithiated (20 mL) and silylated (3.6 mL) following the above-mentioned procedure. Typically, after one relithiation **7** was formed quantitatively (³¹P NMR spectroscopy). The solvent was removed in vacuo. The yellow solid was extracted with hexanes (2 × 100 mL, 50 mL), filtered, and the solvent was removed. The crude product was purified by vacuum distillation (113°C, 0.01 mmHg), affording title compound (6.6 g, 48%) as a colorless liquid.

³¹P NMR (162 MHz, CDCl₃): δ –153 (s); ¹H NMR (400 MHz, CDCl₃): δ 7.50–7.46 (m, 1H), 7.34–7.25 (m, 2H), 7.10–7.04 (m, 1H), 3.98 (sept, ³J_{HH} = 7 Hz, 1H), 1.25 (d, ³J_{HH} = 7 Hz, 6H), 0.30 (s, 9H), 0.28 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.6 (d, J_{PC} = 21.5 Hz), 138.5 (d, J_{PC} = 6 Hz), 130.3 (d, J_{PC} = 11.5 Hz), 128.1, 125.6 (d, J_{PC} = 6 Hz), 124.9, 32.2 (d, J_{PC} = 24 Hz), 23.9, 1.6, 1.4; HRMS calcd for C₁₃H₂₉PSi₂: 296.1546; found: 296.1547; MS (EI): *m/z* (%) 297, 296 [6, 21, M⁺], 282, 281 [2, 6, M-Me], 224, 223 [4, 10, M-SiMe₃], 75, 74, 73 [4, 8, 100, SiMe₃]; Anal Calcd for C₁₅H₂₉PSi₂: C, 60.76; H, 9.86; found: C, 60.42; H, 9.84.

2-*t*-BuC₆H₄P(SiMe₃)₂ (**8**). Same procedure as described above for **7**. Used **6** (4.1 g, 25 mmol), MeLi in Et₂O (1.5 M, 33 mL, 50 mmol) and TMSCl (6.3 mL, 50 mmol). The crude product was purified by vacuum distillation (130°C, 0.01 mmHg) to afford title compound (5.65 g, 72%) as a colorless liquid.

³¹P NMR (162 MHz, CDCl₃): δ –134 (s); ¹H NMR (400 MHz, CDCl₃): δ 7.57–7.53 (m, 1H), 7.48–7.43 (m, 1H), 7.25–7.19 (m, 1H), 7.09–7.03 (m, 1H), 1.62 (d, J_{PH} = 1 Hz 9H), 0.29 (s, 9H), 0.28 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.7 (d, J_{PC} = 18 Hz), 142.6 (d, J_{PC} = 6 Hz), 130.8 (d, J_{PC} = 22 Hz), 127.7, 126.6 (d, J_{PC} = 8 Hz), 124.6, 37.4, 32.0 (d, J_{PC} = 11 Hz), 1.9, 1.8; HRMS calcd for C₁₆H₃₁PSi₂: 310.1702; Found: 310.1701; MS (EI): *m/z* (EI) 312, 311, 310 [2, 9, 32, M⁺], 296, 295 [3, 9, M-Me], 239, 238, 237 [4, 10, 49, M-SiMe₃], 74, 73 [7, 100, SiMe₃]; Anal Calcd for C₁₆H₃₁PSi₂: C, 61.88; H, 10.06; found: C, 61.90; H, 10.09.

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